

HERMES DECLARATION EXHIBIT 15 – PART 3 OF 8

United States Patent [19][11] Patent Number: **4,470,941****Kurtz**[45] Date of Patent: **Sep. 11, 1984****[54] PREPARATION OF COMPOSITE SURGICAL SUTURES****[75] Inventor:** Leonard D. Kurtz, Woodmere, N.Y.**[73] Assignee:** BioResearch Inc., Farmingdale, N.Y.**[21] Appl. No.:** 384,245**[22] Filed:** Jan. 2, 1982**[51] Int. Cl.:** B29B 3/02**[52] U.S. Cl.:** 264/136; 128/335.5;

264/108; 264/134; 264/171; 264/174;

264/288.8; 264/290.5; 264/345

[58] Field of Search 428/397, 375, 372;

425/113, 192 R; 264/174, 562, 108, 288.8,

134-137, 345, 210.8, 290.5, 171, 210.7;

128/335.5

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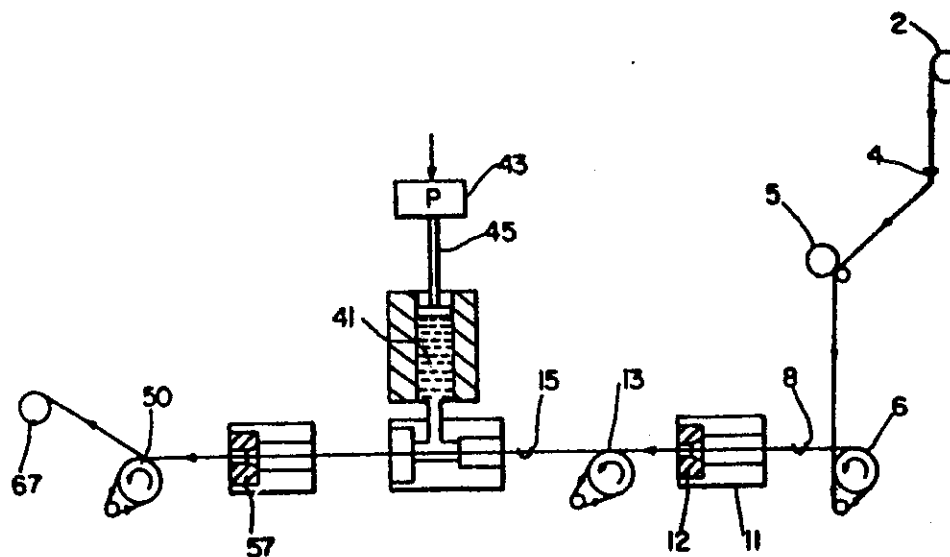
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Primary Examiner—Jeffery Thurlow**Attorney, Agent, or Firm**—Larson and Taylor**[57]****ABSTRACT**

Composite sutures of dissimilar synthetic polymer materials are prepared by forming a thread comprised of a plurality of fibers of a first synthetic polymer, said thread further comprising a second synthetic polymer in intimate association with and present uniformly along the length of said first synthetic polymer, then applying pressure to the softened polymer to redistribute it throughout the plurality of fibers, and into the interstices thereof and sterilizing the thread to form a suture thereof.

33 Claims, 2 Drawing Figures

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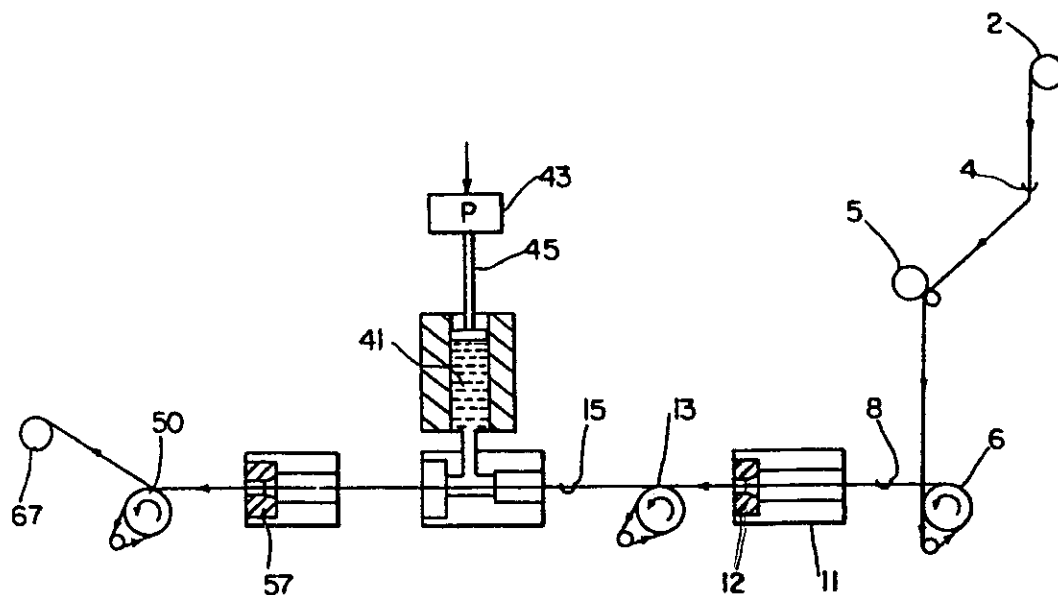


FIG. 1

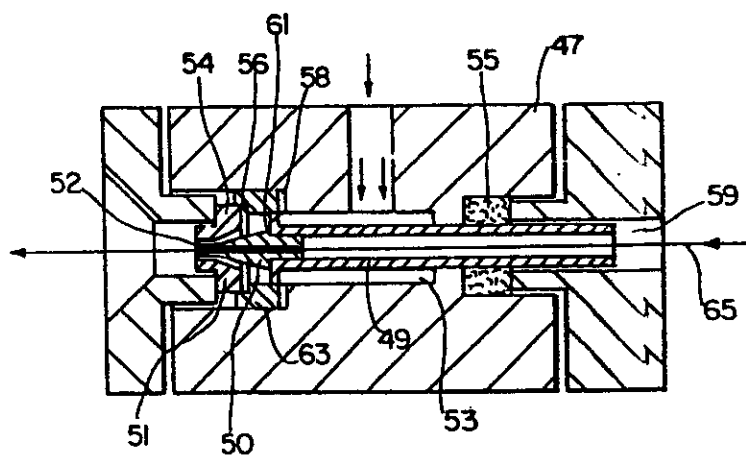


FIG. 2

PREPARATION OF COMPOSITE SURGICAL SUTURES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for preparing composite surgical sutures. More particularly, the invention is directed to methods by which composite sutures of improved lateral strength are obtained.

2. Brief Description of the Prior Art

Composite sutures offer a number of advantages recognized by the prior art. For instance, there are many synthetic fibers which per se are unsuitable for use in sutures because they lack one or more of the properties required in surgical sutures but which possess, nevertheless, certain other properties considered desirable in sutures. By way of example, fibers drawn from many synthetic polymers are too stiff and do not satisfy the knottability requirements of sutures. At the same time these synthetic polymers may possess a tensile strength that renders their use in sutures highly desirable. It is not surprising, therefore, that there have been numerous attempts to combine the best properties of different synthetic materials by compositing them in various ways. These compositing attempts have not been without shortcomings, however.

The principal difficulties involved in the preparation of composite sutures have resided in the fact that polymers whose properties render them desirable for compositing often lack cohesiveness for one another and are otherwise unable to adhere to each other. Many have attempted to remedy these problems by resorting to chemical adhesion through reactive groups provided the polymer components and/or chemical additives to assist in the binding of one polymer component to the other. These techniques, in addition to being costly have in large part proved unsuccessful.

Other attempts to integrate multi-components strands in the production of strings for athletic rackets has been described, for example, in U.S. Pat. No. 4,275,117 to Steven J. Crandall and involves subjecting a fibrous strand composed of fibrous materials having differing melting points to heating conditions sufficient to melt some but not all of the fibrous materials. While perhaps satisfactory for tennis string production or the like, this method of forming composites, as in the case of other aforementioned prior art methods, provides unsatisfactory surgical sutures in that they are found to possess poor lateral strength manifested by a lack of stability against abrasion, kinking and fibrillation during knotting.

Accordingly, it is an object of the present invention to provide a method whereby composite sutures of synthetic polymers having improved lateral strength, that is, composite sutures stabilized against abrasion, kinking and/or fibrillation during knotting are obtained.

Yet another object of the invention is to provide a method of enabling preparation of composite sutures whose surface characteristics, tensile strength and/or knot strength can be tailored to desired specifications.

A further object of the invention is to provide a method of preparing a composite suture whereby one synthetic polymer is tenaciously anchored to the other without the use of chemical adhesion, chemically reactive groups or additives to bind one polymer to the other.

A still further object of the invention is to provide a method for composite suture preparation which enables the use of synthetic fibers heretofore unsuitable for use in suture manufacture.

Another subject of the invention is to provide a method of manufacturing a composite suture having monofilament characteristics which is free of flaking on its outer surface and which retains in large part the flexibility, knottability, knot retention and tensile strength that characterizes multifilament sutures.

SUMMARY OF THE INVENTION

These and other objects of the invention are obtained by forming a thread having interstices therein, comprised of a plurality of fibers of a first synthetic polymer, said thread further comprising a second synthetic polymer in intimate association with and present along the length of at least one of said plurality of fibers, softening said second synthetic polymer to cause flow thereof, applying sufficient pressure to the softened polymer for a time sufficient to redistribute it throughout the plurality of fibers of said first synthetic polymer and into the interstices thereof.

Absolutely essential to the construction of the composite sutures is the pressure step of the method for without it composite sutures having acceptable lateral strength are not obtained. The pressure can be applied to the softened polymer component of the thread in a suitable way with the only proviso being that sufficient pressure be used for a time sufficient to redistribute the softened polymer throughout the fibers of the first synthetic polymer and substantially fill the voids in the thread. According to one preferred embodiment of the invention the pressure is applied by placing the thread under tension during the softening operation. Another preferred method by which the pressure can be applied in the method of the invention is to pass the thread immediately after the softening operation through a compression die having a reduced diameter relative to that of the diameter of the thread so that the necessary pressure can be applied. Although unnecessary, it is preferred in the latter case to use a compression die heated to above the melting point of the polymer component softened. If desired, both forms of pressure application can be utilized as by first effecting the pressure by placing the thread under tension followed by passing the thread through the compression die of reduced diameter.

Since the thread is under pressure, the softened dissimilar polymer exudes into and through interstices existing in the plurality of unsoftened fibers, substantially filling same and forming an internal cast within the matrix of unsoftened fibers upon resolidification. The internal cast of the softened polymer may be continuous or discontinuous and will appear in cross-section in the composite suture as a homogeneous, solid phase throughout the plurality of unsoftened fibers. In most instances, it will be preferred to use an amount of softened polymer sufficient to form upon redistribution throughout the plurality of fibers of the unsoftened synthetic fiber an external cast extending continuously throughout the thread.

Also, where enough of the polymer component softened is present, the liquified polymer exudes through the interstices of the unsoftened fibers and onto the surface of the thread so as to form a coating thereon.

In all instances, however, the internal cast formed within the matrix of unsoftened fibers serves as a tenacious

cious "anchor" onto which additional softened synthetic polymer can be secured as by coating, if desired.

Composite sutures prepared by the present invention having coatings of the exuded synthetic polymer component are preferably smoothed, for instance, by passing them through a heated smoothing die. The smoothed composite thread may then be sterilized if desired to form a surgical suture. In many instances, it may be necessary to further coat the smoothed composite with additional similar synthetic polymer as by extrusion or melt coating to seal and further strengthen the composite thread formed. In addition where the thread is in braided form, subsequent coating tends to eliminate any undulating effect that results as a consequence of the braid and provide a flexible, composite polyfilamentous composite suture having a monofilament-like structure exhibiting improved knottability and knot retention. The improvement in knottability and knot retention characteristics is obtained by virtue of the fact that when a knot is "thrown" and tied down, the suture undergoes a marked deformation in the knot due to the "hills and dales" of the underlying thread.

DETAILED DESCRIPTION OF THE INVENTION

By the term "softening" as used herein and the appended claims is meant any operation by which one of the synthetic polymer components of the thread treated but not the other is brought from a solid or highly viscous state to a viscosity causing flow of the synthetic polymer under the prevailing conditions. This "softening" can be achieved by a variety of ways such as by the use of heat, selective solvents, high energy sources such as lasers, etc. Other suitable ways of effecting the softening will readily come to the mind of those of ordinary skill in this art.

In the aspect of the invention wherein the softening is induced by heating, the thread, comprised of a matrix of a plurality of fibers of a first synthetic polymer and a second solid, dissimilar synthetic polymer having a melting point lower than the melting point of said first synthetic polymer is heated at a elevated temperature sufficient to melt and liquify the dissimilar synthetic polymer, to a viscosity permitting flow throughout the matrix.

Similarly, where the "softening" is induced by a solvent, the thread of dissimilar synthetic polymer components is contacted at a temperature and with a solvent capable of solubilizing or softening the second synthetic polymer but not the first at the contact temperature. The contact time will vary depending principally upon the particular synthetic polymer to be softened and the solvent and contact temperature employed. In all instances, however, the contact time will be sufficient to cause one of the synthetic polymer components to flow, that is, to reduce the viscosity of the polymer to where it flows under the external pressure applied according to the invention and through the remaining, or unsoftened synthetic fibers so as to fill the voids or interstices therein. There is thus formed an internal cast throughout the thread which is dried to resolidify the exuded softened polymer component.

The thread softened in accordance with the present invention can assume a variety of structures and the polymer component to be softened can be present during the softening in any desired form such as a film or fiber, or as a coating on the polymer not softened. In one embodiment, for example, the thread is comprised

of lower melting point synthetic polymer fibers in a plied, twisted, braided or commingled construction with synthetic polymer fibers of higher melting point. A preferred form of this embodiment involves heating under tension a thread comprised of a cover of a polyfilamentous synthetic polymer surrounding a core of at least one but preferably a plurality of fibers of a dissimilar synthetic polymer having a lower melting point than the synthetic polymer of said cover.

Alternatively, the thread to be heated pursuant to the present invention can comprise, at least in part, a plurality of synthetic polymer fibers coated with a dissimilar synthetic polymer having a melting point lower than that of the synthetic polymer fiber substrate, which coated fibers are in a plied, twisted, braided, commingled or simply aligned construction.

The proportions of lower melting point synthetic polymer component to higher melting point synthetic polymer component employed in the thread heated in accordance with the invention will vary depending principally upon the particular components selected, whether or not a continuous or discontinuous internal cast is desired and whether or not a composite coated with melted components is the intended product. In all instances, however, the component melted should be present in amounts at least sufficient to provide adequate anchoring sites for additional like synthetic polymer material that may be subsequently applied as a coating to the composite thread formed.

In general, the ratio of higher melting point synthetic polymer material to lower melting point synthetic polymer material in the initial thread required to achieve adequate anchoring sites is at least 0.5:1 on a volume basis. Ratios of melted to unmelted synthetic polymers in excess of 1:10 up to 2:1 are generally required, however, if it is desired to not only fill all the interstices of the thread but to coat the thread as well. Proportions in excess of about 12:1, can create processing difficulties due to thread line non-uniformities.

Heating of the precursor thread of multiple synthetic polymer components to temperatures above the melting point of one of the synthetic components can be conducted in any suitable manner as by passing it through a suitable oven preferably under an inert gas such as nitrogen. As the composite thread passes through the oven, the synthetic component of lower melting point melts and under the applied pressure exudes through the voids present in the plurality of higher melting fibers remaining leaving them substantially filled. Preferably the softened polymer exudes onto the surface under the tension applied.

Any excess melted synthetic polymer can then be trimmed off manually but it is preferred that the thread structure thus formed be passed through a heated die which trims nubs from the thread and otherwise smooths the external surface of the thread. If the thread thus formed is to be coated, it is important to select a die in this operation which provides a precoated yarn that is at least 20-40 microns thinner than the suture class limits in order to leave room for the coating. Again, it is preferred that this operation be conducted under an inert gas such as nitrogen. Stretch may also be applied during the smoothing operation. The thread may be passed through the heating oven and/or smoothing die as many times as is necessary to obtain a smooth, nub-free surface. Advantageously, in smoothing down the nubs not only should excess surface polymer be removed, but some of it should be used to fill the ups and

downs of the thread's surface in order to obtain a sufficiently smooth undercoat structure. If this is not done, the polymer remaining on the surface follows the contours of the thread and any subsequently applied polymer coating will follow these contours.

The temperature employed in the heating oven will vary depending on the polymer components and the speed at which the thread is passed through the oven. As aforementioned, the temperatures should be raised above the melting point of the polymer of lower melting point to a level at which the polymer melts and reaches a viscosity permitting it to exude through the thread as a gelatinous mass which can then be seen on the surface of the thread when it cools. Excessively high temperatures which then the lower melting polymer to a point where it runs off should be avoided as they tend to exude too much polymer and fail to produce a solid cast structure.

Regardless of the method utilized to induce the required pressure, the actual or optimum pressure applied will vary depending principally upon the particular synthetic polymer components that make up the thread, the softening conditions, the flow viscosity of the softened polymer compound and the nature of the thread construction, i.e. braid, twist, yarn, etc. It is important to note, however, that giving the thread a high level of stretch during the heating operation reduces or eliminates the necessity of applying stretch in any subsequent coating and final sizing stages that may be employed.

The optimum heating temperature employed in a softening operation wherein one of the polymer components is melted will not only depend upon the particular polymer of lower melting point employed but also on the melting point and/or the zero strength temperature of the higher melting polymeric component forming the matrix. In the case of polymers having high crystallinity, the more important consideration is not so much the melting point of the lower melting polymer but rather the temperature at which the polymer reaches a fluidity or viscosity that facilitates exudation. In the case of non-crystalline polymers, on the other hand, only the last criterion applies since non-crystalline polymers do not have a melting point. Usually this temperature is in excess of the melting point of the polymer. For example, to obtain acceptable fluidity with isotactic polypropylene which melts at about 160° C., the polymer should be heated at a temperature within the range of about 180° to 280° C. depending on its molecular weight. Fiber-forming polyethylenes will generally process in the range of about 160° to 275° C. Nylon 66 (polyhexamethylene adipamate) usually will require a heating temperature of about 280° to 295° C. and polyethylene terephthalate a heating temperature of about 270° to 320° C.

Smoothing die temperatures will also be above the melting point of the lower melting synthetic polymer and usually below the melting point of the dissimilar synthetic polymer component. In most instances, the smoothing die temperatures will conform closely to the temperature employed in the heating, i.e. structure formation/precoating stage. Preferably the smoothing die temperature about 5 to 15 degrees below that used in the structure formation/precoating stage.

In a preferred embodiment of the invention, the smooth composite suture structure formed is subjected to coating stage wherein polymer is melt extruded onto the structure. Any of the conventional extrusion apparatuses can be employed for this purpose. The smooth

composite suture structure is simply fed through the extrusion coating die and coated with additional polymer of the same type as used in the structure formation, i.e. precoating stage. Optionally, a smoothing operation can follow this stage using a heated die as described above.

The extrusion temperatures employed in the coating stage depend upon the polymer added and generally will conform to those employed in the heating operation. It has also been found that when the coating is done with apparatus of the melt flow rheometer type the higher the coating temperature, other conditions being equal the greater the finished suture diameter. This is due to decreased melt viscosity with increased temperatures which results in increased polymer flow under a given applied force. The thickness of the polymer coating can be easily regulated by changing the applied extrusion force. If the coated suture is to be subjected to a final sizing operation this thickness should be 30-40 microns larger than the required final size.

After a coating stage, the coated thread preferably undergoes a final size stage. Ordinarily, a thread leaving the coating stage is thicker than the USP size limits. In order to bring it to USP size requirements, a size or calibration process is carried out. The final sizing in such cases is made by passing the coated suture through the calibration die, preferably a non-split die. In addition to its sizing function the calibration die has additional operations: (a) all possible homogeneities in the coating are eliminated (b) squeezing the coated suture through the hot calibration die results in additional co-melting of the polymer in the sheath with the polymer on the surface of the precoated thread, thus improving the adhesion of the coating to the thread and (c) if for some reason the flow rate of the polymer melt changes at extrusion during the coating stage, it results in increased thickness of the coating. The calibration die will control the final thickness by scraping off excess polymer coating.

The coated suture should contact the walls of the calibration die while still in the molten state, in order to prevent abrasion of cold polymer coating passing through the calibration die. The distance between the outlet of the coating die and the calibration die should be minimal in order to secure a coated suture which is sufficiently rigidified so that when it goes through the calibration die it takes the shape of the die but at the same time it should be soft enough to give a smooth finish. Distances of 5 to 7 cm have been found suitable. On leaving the coating die the coating thickness of the suture should be significantly larger (by 30-40 m) than the inner diameter of the calibration die in order that the space in the capillary part of the die and the entrance to the die will always be filled by the polymer melt. On the other hand, too heavy a coating will cool faster leaving the coating die and will not be heated up rapidly enough to pass through the calibration die. This will disturb the scraping action and will produce breaks in the suture or a rough surface.

When softening of the second synthetic is effected by the use of solvent, the solvent selected will depend, of course, upon the nature of the first component of thread treated since the latter must not soften during the operation. The following are illustrative of solvents generally suitable for use in softening exemplary types of synthetic polymers:

Polyesters—mixtures of halogenated hydrocarbons (e.g. methylene chloride) and halogenated alkanols (e.g. hexafluoroisopropanol).

Aromatic polyamides—strong acids and bases

Nylons—phenols

Polyolefins—aromatic hydrocarbons (e.g. xylene, toluene)

The synthetic/polymer components selected for compositing in accordance with the present invention are without limitation provided they are toxicologically acceptable, fiber- or film-forming polymers, possessing softening points sufficiently distant from each other to permit softening of one without softening or otherwise degrading the other. Thus, the synthetic polymers can be thermoplastic or non-thermoplastic polymer materials illustrative of which are homopolymers and copolymers of a olefins of 1-6 carbons, e.g. polyethylene, polypropylene, polybutene, polyisobutylene, copolymers of ethylene and propylene and the like; polyacrylates such as polymethacrylate, polyethacrylate, and the like; polyamides such as Nylon 66, i.e. poly(hexamethylene adipamide), Nylon 610, i.e. (polyhexamethylene sebacamide), Nylon 6, i.e. polycaprolactam; aromatic polyamides, such as those described in U.S. Pat. Nos. 3,063,966; 3,600,350; 3,671,542 and 3,819,587, all incorporated herein by reference, particularly poly(p-benzamide); poly(p-phenylene terephthalamide); poly(2-chloro-p-phenylene terephthalamide); poly(2,6-dichloro-p-phenylene-2, 6-naphthalamide); poly(p-phenylene-p,p-biphenyldicarboxamide); poly(p, p'-phenylene benzamide and poly(1,5-naphthylene terephthalamide); copoly(p,p'-diaminobenzanilide terephthalamide); polyesters of difunctional carboxylic acids and diols such as polyethylene terephthalate, poly(1,4-cyclohexylene dimethylene terephthalate); polystyrene; poly(acrylonitrile); polyurethane, polyethers, polyvinyls, polypeptides such as polylactides, polyglycolides and copolymers of lactide and glycolide with each other and with other reactive monomers such as those described, for instance, in U.S. Pat. Nos. 3,636,952 and 2,683,136, incorporated by reference herein; and polymers of p-aminobenzoic acid.

Illustrative of suitable composite threads for treatment in accordance with the present invention are set forth in the following Table I:

TABLE I

Composite	Matrix	Extruding Polymer
1	polyethylene terephthalate	isotactic polypropylene
2	Kevlar ⁽¹⁾	polypropylene
3	Kevlar ⁽¹⁾	polyethylene
4	Kevlar ⁽¹⁾	polyethylene terephthalate
5	chain extended polyethylene ⁽²⁾	atactic polypropylene
6	Kevlar ⁽¹⁾	polyglycolic acid
7	Nylon 66	isotactic polypropylene
8	Nylon 66	polyisobutylene
9	polyethylene terephthalate	Nylon 11

⁽¹⁾aromatic polyamide product of DuPont Corporation

⁽²⁾high strength polyolefin yarn having straight pull tenacity of approximately 25-30 g/denier described in Keller A. and Barham, P. J., "High Modulus Fibres", Plastics and Rubber International, Feb. Vol. 6, No. 1 (1981) incorporated herein by reference.

The following examples are included to further illustrate preparation of composite sutures of the invention. In the examples, reference is made to the following brief description of the drawings wherein:

FIG. 1 is a schematic drawing of an apparatus useful in the three stage melting method of the present invention and

FIG. 2 is a schematic drawing in section of a spinneret useful in the extrusion coating of the formed composite suture employed in the apparatus of FIG. 1.

EXAMPLE I

Structure Formation or Precoating Stage

Directing attention to the drawings, using a conventional New England Butt braider machine polyethylene terephthalate (PET) strands of 40 denier are braided around a single core of 265 denier isotactic polypropylene to form a 4/0 raw or precursor thread with 4 ends of 40 denier PET in the cover and 1 end of 165 denier polypropylene in the core. The raw braid, wound around a reel 2, is fed through a guide 4, between nip rollers 5 about a feed roll (Godet) 6, through guide 8 into a heated 10 cm long tubular over inside Spinneret I designated 11 in FIG. 1. The lumen of Spinneret I without polyolefin feed serves this purpose, Heated Zone I in FIG. 1. A roll (Godet) 13 pulls the raw braid through the oven at a stretch ratio (SR) of 1.24. The heating oven is maintained at a temperature of 230° C. Under these conditions all the polypropylene melts and is entirely distributed throughout the braid interstices and onto the surface of the braid. No solid polypropylene core residue remains.

As the braid emerges from Spinneret I, large quantities of excess polypropylene which has melted out and formed nubs on the surface is trimmed off by a smoothing die 12 having an internal diameter (ID) of 0.180 mounted at the outlet of Spinneret I. The braid then continues through a Guide 15 to Spinneret II designated 39 which is an extrusion coating die apparatus shown in detail in FIG. 2.

Coating Stage

The smoothed precoated braid is pulled through Spinneret II by a roll (Godet) 50. Tension is let down on roll 50 so that some overfeed, i.e. a stretch ratio (SR) of approximately 0.9 is applied. Isotactic polypropylene chips are melted in heated reservoir 41 maintained at a temperature of 260° C. and the melt is forced by means of extruding weights 43 applying a force of 0.233 kg to a piston 45 into and through the tubing-type extrusion coating die apparatus 39.

Directing particular attention to FIG. 2, the extruding coating apparatus 39 is comprised of a holder indicated generally as 47 which houses a hollow guide tube 49 and a die holder 50 which retains a die 51. Die 51 has an outlet 52. The guide tube 49 is essentially positioned within the holder 47 so as to provide an annular chamber 53. A Teflon gasket 55 seals one end of the guide tube 49 within the holder while the other end is connected to die 51 and sealed by aluminum gaskets 54, 56 and 58. The guide tube contains an inlet 59 and an outlet 61. Between outlet 61 and outlet 52 of the die 51 is positioned a hollow needle 63. The polypropylene melt from heated reservoir 41 is forced by piston 45 through channel 65, into annular chamber 53 and over needle 63. The impregnated/precoated thread 65 passes consecutively through guide tube 49, hollow needle 59, outlet 52 and is coated with the melt as it emerges from the die 51. The coating die is maintained at a coating temperature of 230° C.

Final Sizing or Calibration Stage

The coated thread is passed to a Spinneret III designated 66 whose design is like that of Spinneret I except that a calibration die 67 (see FIG. 1) having an internal diameter of 0.220 mm is employed so as to provide a finished 4/0 suture. Spinneret III is positioned approximately 5 cm from the outlet of Spinneret II so as to provide a coated thread cooled to a rigidity that allows the coated thread when it enters Spinneret III to take the shape of calibration die 67 but is soft enough to give a smooth finish. The working temperature of Spinneret III is 220° C. Some overfeed (Stretch Ratio, SR approximately 0.9) is applied in the finishing stage as in the coating stage so as to improve the smoothness of the final product.

The finished suture is finally wound around receiving reel 69 and identified in the Table II below as CK suture 4-0.

Sutures of 3-0, 5-0 and 6-0 diameter size were similarly prepared and the mechanical properties of these sutures, identified below as CK sutures 3-0, 5-0 and 6-0 as well CK Suture 4-0 are reported in Table II. Also included for purposes of comparison are the mechanical properties of commercial sutures of like size.

TABLE II

No.	Type of Suture	Knot-pull Tensile Strength, F_{knot} (g)		Percent Elongation (%)	Knot Security		Gurley Stiffness O.S. (mg)
		Required by USP*	Measured		K_{ave}	$n_2/n_1 - 1/5$	
1	CK Suture 3-0	1200	1436	15.0	2	—	8.2
2	Prolene 3-0 (from Ethicon)	"	1504	58.3	3	$n_2/5 = 5$	19.8
3	PP Yellow Monofil. 3-0 (from Thiokol)	"	1430	39.4	3	$n_2/5 = 5$	24.9
4	Nylon White Monofil. 3-0 (from Deknatel)	"	1434	50.4	4	$n_2/5 = 5$	22.8
5	PET Monofil. 3-0	"	2430	76.1	3	$n_2/5 = 5$	32.0
6	CK Suture 4-0	750	930	12.8	2	—	5.9
7	Prolene 4-0 (from Ethicon)	"	946	56.7	3	$n_2/5 = 5$	9.9
8	PP Blue Monofil. 4-0	"	841	29.1	3	$n_2/5 = 5$	14.4
9	Nylon White Monofil. 4-0 (from Deknatel)	"	950	47.8	4	$n_2/5 = 5$	12.4
10	PET Green Braid Suture 4-0	"	1146	16.5	4	$n_2/5 = 1$	3.0
11	CK Suture 5-0	500	649	14.2	2	—	2.2
12	Prolene 5-0 (from Ethicon)	"	646	44.9	3	$n_2/5 = 5$	3.1
13	PP Blue Monofil. 5-0	"	532	31.5	3	$n_2/5 = 5$	5.9
14	Nylon White Monofil. 5-0 (from Deknatel)	"	577	51.0	4	$n_2/5 = 5$	5.4
15	PET Green Braid Suture 5-0 (from Deknatel)	"	770	25.2	4	$n_2/5 = 1$	0.6
16	Suture 6-0	250	318	11.0	2	—	0.4
17	Prolene 6-0 (from Ethicon)	"	270	50.0	3	$n_2/5 = 4$	0.6
18	PP Blue Monofil. 6-0	"	192	29.9	3	$n_2/5 = 5$	1.1
19	PET Monofil. 6-0	"	485	37.0	3	$n_2/5 = 5$	3.3

*The limits on F_{knot} apply to non-sterile sutures.

RESULTS

Knot-Pull Tensile Strength

Sizes 3-0, 4-0 and 5-0 CK Sutures have the same F knot as Prolene and Nylon Monofilaments (the differences being within the limits of 3% except for Nylon 5-0 which is 12% weaker than CK Suture 5-0). It should be noted that the values of 5-0 sutures are 20-30% higher than required by U.S.P. In size 6-0 the F knot of the CK Suture is 18% higher than that of Prolene. PP monofilament (blue) is remarkably weaker than the CK Suture (the difference increases from 11% in size 4-0 up to 66% in size 6-0).

PET sutures have F knot values higher than CK Sutures. PET Monofilaments of 3-0 and 6-0 have F

knot values 50-60% higher than CK Sutures of the same size. For PET Braid Suture 4-0 and 5-0 the difference is about 20%.

Gurley Stiffness

By comparing all materials having the same 3-0 size (samples 1-5, all of them monofilaments) it is seen that the CK Suture 3-0 has the lowest Gurley Stiffness (G.S.). Size 3-0 polypropylene monofilaments (Prolene from ethicon and PP from Thiokol) and nylon monofilament (from Deknatel) have G.S. 2.5-3 times higher than that of similarly sized CK Suture. PET 3-0 monofilament has the highest G.S. — 6.3 times higher than that of the CK Suture.

When comparing G.S. of size 4-0 materials (samples 6-10) it can be seen that the G.S. of Prolene 4-0 is still remarkably higher (by 68%) than that of the KC Suture but, on the other hand, the G.S. of PET 4-0 multifilament suture from Deknatel is two times lower than that of CK Suture 4-0. Such a result is not surprising when comparing the stiffness of multifilament with monofilament yarns.

In the size 5-0 the G.S. of CK Suture is 39% lower than that of Prolene, but 3.9 times higher than that of PET 5-0 multifilament.

It may be safely stated that, when comparing CK Suture with other sutures of the same size, the G.S. of CK Sutures is remarkably lower than that of Prolene, PP, PET and Nylon monofilaments. This difference is particularly high when comparing with PET monofilaments of the same size. On the other hand, the G.S. of CK Sutures is remarkably higher than that of PET multifilament sutures. This results from the structure of CK Sutures.

Elongation

The P.E. of CK Sutures of all sizes varies from 11% to 15%. The P.E. of other monofilament sutures is much higher, for example: P.E. of Prolene in all sizes varies

from 43% to 58%; of PP monofilament from 29% to 39%; of NNylon monofilament from 41% to 51%; and of PET monofilament from 37% to 76%. Only P.E. of PET monofilament suture 4-0 (16.5%) is close to the desired variance.

Knotability

Knotability results show that the CK Suture has the lowest stiffness and elongation when compared with other monofilament sutures. It can, therefore, be stated on the basis of these two quantitative parameters, that the knotability of the CK Suture is better than that of any other monofilament suture.

Knot Security

It may be seen from the Tables that all investigated materials can be divided into 3 groups with corresponding k_{sec} = 2, 3 and 4. CK Sutures belong to the group with k_{sec} = 2. All Prolene sutures, PP monofilaments and PET monofilaments belong to the second group with k_{sec} = 3. PET braids and nylon monofilaments belong to the third group with k_{sec} = 4. It means that with CK Sutures, a secure knot can be tied using only two throws Square Knot. All other investigated materials need at least one additional throw for secure knot formation and nylon monofilaments and PET braids need even two additional throws.

Micronscopic examination (250X) of a cross-section of the finished suture shows virtually no dead spaces present. The finished suture is free of stripping and cracking and possesses the smoothness of a monofilament.

In commercial production, needles may be attached to one end of the composite sutures of the invention and the sutures may be packed in sterile containers. Inasmuch as the sutures are stable for long periods of time without a conditioning fluid, the sutures may be dry packed in glass tubes or plastic envelopes. Conditioning fluid may be used to assure maintenance of sterility or as a lubricating medium for the needle. Eyeless needles are preferred since they cause less tissue damage. Conveniently, the composite sutures of the present invention are formed at convenient lengths, attached to eyeless needle, wound on reels if desired, and placed in containers such as plastic envelopes. The sutures may then be sterilized with ethylene oxide or other conventional gaseous sterilizing agents in accordance with known practices. Alternatively, the sutures may be sealed in the envelopes and then sterilized by using heat and radiation including x-rays, gamma rays, electrons, neutrons, etc.

EXAMPLES II-IX

Example I is repeated using the following synthetic materials as the matrix and core, i.e. lower melting point component and conducting the heating in Heating Zones I and II as indicated.

Ex- am- ple	Matrix	Core	Spinneret I, °C.	Spinnerette II & III, °C.
II	Kevlar ⁽¹⁾	isotactic polypropylene	220	220
III	Kevlar ⁽¹⁾	polyethylene	225	220
IV	Kevlar ⁽¹⁾	polyethylene terephthalate	265	265
V	chain extended polyethylene ⁽²⁾	isotactic polypropylene	70	45
VI	Kevlar ⁽¹⁾	polyglycolic	238	230

-continued

Ex- am- ple	Matrix	Core	Heating Zone I, °C.	Heating Zone II, °C.
VII	Nylon 66	isotactic polypropylene	230	222
VIII	Nylon 66	polyisobutylene	300	190
IX	polyethylene terephthalate	Nylon 11	237	237

(1) S: Table I, supra
 (2) S: Table I, supra

It is claimed:

1. A method of preparing a surgical suture comprising forming a thread having interstices therein, comprised of a plurality of fibers of a first synthetic polymer, said thread further comprising second synthetic polymer in intimate association with and present along the length of at least one of said plurality of fibers, said second synthetic polymer having a lower melting point than said first synthetic polymer, heating the thread to a temperature sufficient to liquify the second synthetic polymer but not the first synthetic polymer to cause flow thereof, placing the thread under tension during said melting to compress the thread and redistribute the liquified second polymer throughout the plurality of fibers of said first synthetic polymer so as to substantially fill the interstices of said thread, said liquified polymer being present during said redistribution in an amount sufficient to exude through the interstices of the unmelted fibers and onto the surface of the thread to form a coating thereon and to form an internal cast extending throughout said thread, said internal cast forming an anchor onto which additional second synthetic polymer can be secured, if desired, and sterilizing the resulting thread to form a surgical suture.

2. A method according to claim 1 wherein the second synthetic polymer is in fiber form.

3. A method according to claim 1 wherein the first synthetic polymer is aromatic polyamide.

4. A method according to claim 3 wherein the aromatic polyamide is poly(p-phenylene terephthalamide).

5. A method according to claim 3 wherein the aromatic polyamide is poly(1,4-benzamide).

6. A method according to claim 1 wherein the first synthetic polymer is chain extended, polyethylene having a straight pull tenacity of about 30 to 50 grams/denier.

7. A method according to claim 3 wherein the first synthetic polymer is polyester.

8. A method according to claim 7 wherein the polyester is polyethylene terephthalate.

9. A method according to claim 1 wherein the second synthetic polymer is polyolefin.

10. A method according to claim 9 wherein the polyolefin is polyethylene.

11. A method according to claim 9 wherein the polyolefin is polypropylene.

12. A method according to claim 1 wherein said coating is subjected to smoothing.

13. A method according to claim 12 wherein said smoothing is effected by passing the composite after said heating through a heated smoothing die.

14. A method according to claim 1 wherein the composite formed is coated with the same synthetic polymer as said second synthetic polymer.

15. A method according to claim 14 wherein the coated composite is subjected to smoothing.

16. A method according to claim 15 wherein said smoothing is effected by passing the composite after said heating through a heated smoothing die.

17. A method according to claim 1 wherein the second synthetic polymer comprises at least one fiber.

18. A method according to claim 17 wherein the second synthetic polymer is polyolefin.

19. A method according to claim 18 wherein the polyolefin is polypropylene.

20. A method according to claim 19 wherein the polyolefin is polypropylene.

21. A method according to claim 1 wherein the first synthetic polymer is a polyamide terephthalate.

22. A method according to claim 21 wherein the polyamide is aromatic polyamide.

23. A method according to claim 22 wherein the aromatic polyamide is poly(p-phenylene terephthalamide).

24. A method according to claim 22 wherein the aromatic polyamide is poly(1,4-benzamide).

25. A method according to claim 21 wherein the polyamide is poly(hexamethylene adipamide).

26. A method according to claim 21 wherein the polyamide is polycaprolactam.

27. A method according to claim 21 wherein the polyamide is poly(hexamethylene sebacamide).

28. A method according to claim 20 wherein the polyamide is poly(w-aminoundecanoic acid).

29. A method according to claim 1 wherein the first synthetic polymer is polyester.

30. A method according to claim 29 wherein the polyester is polyethylene terephthalate.

31. A method according to claim 1 wherein the first synthetic polymer is extended polyethylene having a straight pull tenacity of about 30 to 50 grams/denier.

32. A method according to claim 1 wherein the first synthetic polymer is polypropylene, the second synthetic polymer is polyethylene terephthalate and the softening achieved by heating the composite to a temperature of about 180° to 280° C.

33. A method according to claim 1 wherein the first synthetic polymer is polyethylene terephthalate the second synthetic polymer is polyethylene and the softening is achieved by treating to a temperature of about 160° to 275° C.

* * * * *

June 8, 1965

A. GLICK

3,187,752

NON-ABSORBABLE SILICONE COATED SUTURES AND METHOD OF MAKING

Filed April 27, 1962

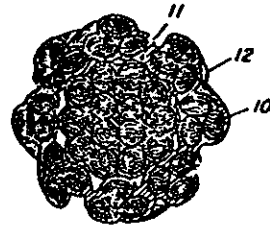


Fig. 1

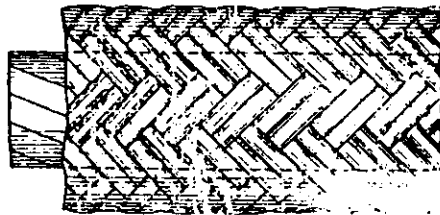


Fig. 2

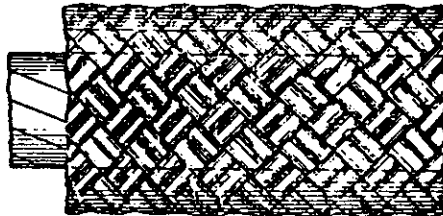


Fig. 3

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DePuy Mitek, Inc. v. Arthrex, Inc.
C.A. No. 04-12457 PBS

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3,187,752
NON-ABSORBABLE SILICONE A COATED SUTURES
AND METHOD OF MAKING

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Filed Apr. 27, 1962, Ser. No. 194,604
26 Claims. (Cl. 122-335.5)

This application is a continuation-in-part of application Serial Number 767,502, filed October 16, 1958 and now abandoned.

This invention relates to a non-absorbable densely constructed suture built up of a plurality of filaments having a serum-proof, moisture-resistant coating on the surface of the individual filaments, which coating contains a silicone resin.

As used in this specification the term "suture" is intended to include both sutures, and are used for the sewing of tissues, and ligatures are used for tying off blood vessels, etc. Different portions of one strand may be used for both purposes in the same operation depending upon the needs of the surgeon at the particular moment.

In surgical practice; and for present purposes, this includes both human and animal surgery, two classes of sutures are commonly used. One is the absorbable suture which is absorbed by the tissues and accordingly loses its identity, such sutures usually being of catgut, etc.; and the other form is a non-absorbable suture which in most instances is permitted to remain as such permanently in the tissues, but which is sometimes removed from the tissues at an appropriate phase of the healing process. Such non-absorbable sutures must be strong and should maintain their strength and integrity for prolonged periods while in contact with body tissues and fluids. It is desirable that such sutures be inert, causing a minimum of tissue irritation, and that the diffusion of fluids through the suture by capillarity be at a minimum.

It has been customary to use silk sutures built up as by braiding, weaving, twisting or spinning, hereafter called coordinate configuration, of from a plurality of individual silk filaments. Synthetic polymers may be used instead of natural silk. These filaments present a construction in which there are fine interspaces which by capillary action cause fluids to travel along these length of the suture. This may permit migration of pathogenic organisms.

Accordingly, such sutures have been coated with waxes, such as beeswax, or beeswax mixed with ethyl cellulose, which material reduces the capillarity of the suture and improves the handling characteristics of the suture.

There is some evidence that under some conditions these waxes cause granuloma formation, and have other undesirable side effects.

Additionally the coating material should be inert to all body fluids and heat stable to permit heat sterilization of the suture. It is desirable that the coating be economical and readily applied.

In addition to the physiological properties of inertness the characteristics of handling and of strength of a suture are extremely important. It is desirable that a suture be sufficiently stiff that it can be easily handled and yet readily formable to a new position. After being bent to a new position, it should maintain this new set position. Many fibrous materials have a plastic "memory," and after being bent to a new position slowly on standing tend to go back to their former shape. A suture should not have plastic "memory" but should when once set maintain that new position.

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Additionally the suture should be easy to tie into a knot and should be resistant to knot-slippage under tension and the knot should remain secure and not slip or untie itself on standing. Additionally, a suture should have what is known as "throwability." That is, the surgeon should be able to pick up the suture and throw it into a new position, which position is then retained. It is desirable at times to place a suture in a given location or throw it in a given direction with the knowledge that the suture will stay there until positively moved.

In the past a great deal of the handling characteristics have been imparted to a limp suture by the coating material. Beeswax or beeswax mixed with ethyl cellulose used as a coating is responsible for the desirable handling characteristics.

If some other coating material is used with the same filament construction, the sutures may not have satisfactory handling characteristics.

It has now been found that by braiding a suture with a tighter and more dense construction using fewer plies, i.e. cross-overs per inch, and by dry stretching the braided filaments, a suture can be formed which has inherently stiffer qualities and improved handleability.

Silk is the usual material used for non-absorbable sutures. Synthetic filaments such as nylon, polypropylene, "Orlon," polyacrylonitrile, "Dacron," a stretched oriented polyester of ethylene glycol and terephthalic acid, etc., or cotton, or linen are sometimes used. Occasionally such materials as stainless steel or monel metal are used. All such materials can be advantageously coated with polymeric silicones, in accordance with this invention, and are braided or spun or formed more tightly for coating with silicones than with conventional coating materials.

Polymeric silicones are applied to this dense suture; such polymeric silicones readily coat the individual filaments increasing the resistance to aqueous fluids without reducing capillarity. Furthermore, such silicones applied as a coating are heat stable. In at least some instances the coating may be applied in a partially polymerized state and the silicone further polymerized in position on the suture. Fortunately and fortuitously, polymerization catalysts are decomposed by heat sterilization procedures or heat curing so that even if toxic catalysts are used as a component of the silicone containing, the final product is completely inert.

The particular silicone resin themselves are not a part of this invention and standard commercial resins may be used. It is not necessary that the material be applied as a liquid, as some of these silicone resin forming materials, such as the General Electric "Dellumet," are volatile and may be applied in the gaseous phase. These materials are among the volatile silicone compounds such as alkyl silicone halides. A material such as dimethyl silicone dichloride is comparatively volatile and may be applied either direct or by allowing it in an ethereal solution thereof to evaporate and the vapor contact the suture material.

Frequently, it is more convenient to use a liquid preparation. Such preparations are solvent dispersions of "silicone resins," that is partially polymerized products which will polymerize to a silicone film. For purposes of convenience it is normally easier to purchase the material under trade names rather than making it, or obtaining it to a performance specification. Materials which are sold commercially such as the Dow-Corning silicone "TDC 803" or "DC 804" or General Electric's "9980" give highly satisfactory and useful films. To those skilled in the art of silicone compounding it is comparatively simple to select a heat-curable or potentially heat-curable silicone resin, which either from its inherent characteristics, or

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the addition of a polymerizing catalyst, will set up or cure. As a final check to insure the complete removal of all halide to silicone linkages, ammonia fumes may be used. Usually sufficient moisture is present to insure the hydrolysis of the halogen, but ammonia fumes insure a neutral product. If desired, silicone containing resins may be used in which the silicone atoms are linked through nitrogen, from ammonia, rather than through oxygen as in the silicones, such resins at times being referred to as silamines.

Methods for preparation of silicone resins are well known. Patent No. 2,306,222 to W. I. Patnode, "Method of Rendering Materials Water Repellent," discloses the use of a vapor of an alkyl silicone halide for making glass vapor-proof. The same types of materials as therein described may be used to water-proof and treat sutures. The patent to Safford, No. 2,424,853, and the patent to Tanis, No. 2,408,822, additionally describe siliceous halides and their conversion to resins. There are several methods of preparing such silicone resins, among others are the reaction of Grignard type reagents with a silicone tetrachloride. From the standpoint of costs silicone tetrachloride is normally used and the Grignard may be either alkyl or aryl or a mixture thereof. The amounts of alkyl and aryl groups used affect the brittleness and rate of cure of the resin formed. Normally the product of the reaction of the Grignard reagent with silicone tetrachloride is allowed to react with moisture, allowed to partially polymerize, and the partially polymerized materials are dissolved in a suitable solvent whereby additional polymerization is either inhibited or substantially slowed down. The higher the ratio of lower alkyls, the more rapid the materials will cure and the more brittle will be the film. The more highly branched the chains formed in the resin, which are necessarily formed by the polymerization of the silicone types containing more halide atoms per silicone molecule, the more brittle and polymerized are the resins.

The organo-silicones sometimes referred to as organopolysiloxanes, more particularly the hydrocarbon substituted polysiloxanes are particularly suitable for suture coating. The patent to Wright et al., No. 2,339,477, entitled "Polysiloxane Resins" gives considerable information of this type of resin. Certain of the resins which are described in the patent to Hyde, No. 2,386,466, "Insulated Conductor and Insulation Therefor," if diluted with a solvent may be used in accordance with the instant invention. The patent to Hyde, No. 2,371,050, "Organosilicone Polymers and Method of Making Them," describes certain additional methods of preparing such resins. It is not necessary that the resins be prepared from halogen containing compounds as, for example, methods such as set forth by Strain et al. in Patent No. 2,394,642, "Silicic Acid Esters," describes a different form of silicone containing resin. The patent to Her, No. 2,395,350, "Modified Alkyd Resins," describes still further modifications of silicone containing resins in which the silicone linkages are different than those classified as organopolysiloxanes.

It is not intended that a treatise be here included on the production of such resins, as such resins are the invention of others and are adequately described in the patent literature, as well as elsewhere. The texts "Introduction to the Chemistry of the Silicones," Eugene G. Rochow, John Wiley & Sons, Inc., New York, 1946, and "Silicones and Their Uses," Rob Roy McGregor, McGraw-Hill Book Company, New York, 1954, give many useful details.

A pamphlet "Silicones in Medicine and Surgery," Rob Roy McGregor, Dow-Corning Corporation, 1957, discloses some of the silicones which may be used, and other medical usages for such silicones.

The silicone acts as a protective layer on the surface of the filaments, and prevents dyes or the surface characteristics of the filaments, such as silk, from interacting

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with body fluids. In neural surgery, suture materials frequently deleteriously affect regeneration of nerve fibers. Silicone coated silk is the first material known to have been successfully used in suturing nerve fibers which permits the regeneration of the nerves in the spinal column.

Usually silk is braided loose enough for a beeswax coating to impregnate the silk, reduce capillarity, and impart desirable handling qualities. The new silicone coating may not inherently have enough body to give the desired handling qualities. Rather than use a more highly polymerized silicone resin, which is stiffer, it is preferred to use a denser silk construction, with more silk filaments in a given cross-section. This gives a greater strength, and a thinner silicone coating gives a proper inertness to the suture and at the same time prevents capillarity.

One standard test for capillarity is to boil two 3 to 4 inch lengths of the suture in distilled water in a glass container for three successive 20-minute periods, changing the water each time. After the third boiling, the test sutures are allowed to stand for at least 8 hours in an atmosphere having a relative humidity of $65\% \pm 2\%$ at a temperature of $21^\circ \pm 1^\circ$ C. The segment of suture is tied to a piece of white silk thread with a square knot, the ends cut close, and suspended by the white silk thread so that the suture dips into a 0.5% aqueous solution of methylene blue, with the knot $\frac{1}{8}$ -inch above the dye solution. After standing for 24 hours, the white silk is inspected for evidence of dye carried up the suture by capillary action. If the white silk is free from dye color, the suture is non-capillary, and passes the test. Both of the duplicate samples should pass.

Sutures of this invention pass this test for capillarity. Sutures which pass this test are non-capillary in tissues of man and animals.

For preventing slippage at knots in the suture, a coating forming a hardened, but flexible silicone film is preferred, using a silicone having a higher ratio of aryl groups. For instance, a polysiloxane having from about 72% to 67% methyl substituents and from 28% to 33% phenyl groups cures to a non-slipping finish that gives excellent knot retention. Usually the suture breaks before the knot slips. Also such polysiloxanes are sufficiently adhesive that spun sutures of silk or other filaments do not unravel, or "broom," and can be threaded into needles.

The silk construction itself rather than the coating can be used to give the handling qualities.

Whereas the number of ends, and total denier, varies with size, it is desirable that a maximum size, and strength be obtained within the overall limits of suture diameter. For the standard United States Pharmacopoeia sizes (United States Pharmacopoeia Convention, Inc., Distributed by Mack Publishing Co., Easton, Penn., elsewhere abbreviated U.S.P.) this is:

U.S.P. size	U.S.P. diameter, inches, max.	Picks per inch	Denier of raw silk used
4-0	0.004	40	112
3-0	0.005	40	162
2-0	0.006	40	178
00	0.008	40	228
0	0.010	40	258

The picks per inch are the number of threads, running in one direction, per lineal inch of suture.

The silk is braided using a smaller number of picks than conventional, and with a larger core size. The braided silk is washed to degum, then dyed, if desired, in skeins in accordance with conventional practice. The silk is dried, and then dry stretched from about 6% to about 11% of its length. This stretching tightens the braid, and gives a more dense, more handleable silk. At least some of the stretching may be accomplished while the silk is wet.

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After stretching the silk suture is passed through a solvent bath containing the polymeric silicone. Such solvents as xylene, toluene, benzene, gasoline, or other non-toxic volatile hydrocarbon solvents may be used. In addition to the silicone, beeswax, ethyl cellulose or a low molecular weight polyethylene may be dissolved and used as part of the coating. For the silicone rubbers, a catalyst is usually used to accelerate the curing rate. The standard organic peroxides, of which benzoyl peroxide is the most frequently used, are suitable catalysts, 2% to 20% by weight of the polymer gives good results. The heat which sets the resin decomposes residual peroxides to give non-toxic products. For the hardened, flexible films, having a higher percentage of phenyl groups, heat alone can cure the silicone. Organo metallic driers such as zinc octoate, or iron stearate accelerates the cure. Non-toxic salts of metals with fatty acids are effective.

A 2% to 50% solids bath gives a satisfactory coating. A 5% to 30% solids concentration in the bath results in easier operating control. A 20% concentration is usually preferred. While an adequate pick up with a single coating bath is obtainable, more uniform distribution and coating can be obtained by using two or more baths, with heat curing between coatings. A cure temperature of at least 150° C. for 30 seconds gives a cure, although longer times at lower temperatures, or a longer cure with less catalysts, etc. in accordance with standard practice in the silicone art may be used.

A total weight of coat of 2% to 20% by weight of the fiber gives good characteristics. This percentage is called the pick up.

The sutures are shown in the attached drawings:

FIGURE 1 is a cross-section of a silicone coated suture.

FIGURE 2 shows a portion of an eight carrier on a 16 capacity carrier braider formed braid.

FIGURE 3 shows a portion of a sixteen carrier braid.

EXAMPLE 1

A silk suture is braided, using 8 carriers, on a sixteen carrier braider, with 3 ends of 13 to 15 denier silk per carrier, and a core of 3 ends of 13 to 15 denier silk, and 40 picks per inch, giving the skipped braid of FIGURE 2. The raw silk used has a total of about 378 denier. (The denier is the weight in grams of 9000 meters of the strand.) The braided suture is washed to degum, then dried, while looped in skeins. The dry silk is stretched 9% of its length, which gives improved stiffness; and increases the density.

A silicone rubber sold as "Silastic 9711" by Dow-Corning is milled into sheets of about 1/4-inch thick, and thereto while milling additionally is added 8.46% by weight of the rubber of a silicone fluid containing 50% by weight benzoyl peroxide (Lupercel ASF). After milling for an additional 5 minutes, the sheets are cut into small pieces and soaked overnight in xylene. The swollen silicone is stirred to a cream-like consistency, then diluted to 20% solids, and stirred until uniform.

The braided silk is immersed in a trough of the silicone solution at room temperature, then wiped over a piece of white felt. The coated silk is passed through a three stage heating tunnel, so that the silk is heated for one minute each at 100° C., 125° C., and 150° C. The silk is spooled after air cooling.

This coating procedure is repeated. In the double coating, the silk is found to have picked up 15% by weight of the silicone coating.

The finished suture gauges 0.0077 inch in diameter and is a 4-0 suture.

A conventional braiding of a 4-0 suture gives about 60 to 70 picks per inch, and uses 8 carriers with 2 ends of 21-22 denier each, and no core. Such a silk suture has a total denier of about 336, and if coated with beeswax in accordance with conventional practice gauges .0085 inch.

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Other characteristics for comparison are:

	Silk With New Silicone	Silk With Old Silicone
Picks per inch.....	40	60
Gauge.....		
Raw.....	.0076	.0081
Sterilized.....	.0077	.0083
Straight pull strength.....	2.77	2.00
Knot pull strength.....	2.94	1.80
Flexibility to bend, 180°.....	.137	.100
816 denier—100% self support.....		
Horizontal (sterile).....	2.04	4.75
Vertical (sterile).....	4.00	5.15
Apparent density as braided.....	1.137	0.927

The increase in strength after sterilization both straight and over a knot shows the new silicone construction to have marked advantages.

The suture is sterilized either by conventional autoclaving procedures, or by ethylene oxide gas, in accordance with commercial practice in the industry.

The individual silk filaments of the braid are shown at 10, the filaments of the core are shown at 11, and the suture has a silicone coating 12. FIGURE 2 shows the construction of a 000 suture, otherwise the same as above.

EXAMPLE 2

The coating of the suture of Example 1 is repeated using a 15% solids solution of a dimethyl silicone polymer of the general formula $((CH_3)_2SiO)_n$ with 5% by weight of the polymer of benzoyl peroxide as catalyst. After two coatings, a readily handleable suture is obtained.

EXAMPLE 3

A multi-filament 4-0 sized silk suture braided as in Example 1 is washed and dyed black in accordance with conventional procedures. The suture is then dry stretched. An alkyl polysiloxane sold by General Electric as "TS-188" is diluted with toluene to form a 10% silicone solids solution. The silk suture is immersed in this solution of the silicone resin at 50° C., then drawn through a curing tunnel at a temperature of 130° C., and of such length as to heat the silk suture for two minutes. The suture may be heated longer, so as to sterilize the suture at this time after which it is sterily packed and handled until used by the surgeon; or after the two-minute heating, the suture may be reeled and packaged using clean but not sterile techniques and finally sterilized by dry heat after packaging and prior to sale, or just prior to use by the surgeon.

EXAMPLE 4

A 4-0 silk suture braided, washed, and dried as described in Example 1 is immersed in a 10% solids solution of the polymerizing silicone resin commercially known as Dow-Corning 804. This resin is a comparatively short chain silicone resin containing both phenyl and methyl substituents on the silicone atoms. The silk suture is immersed in the solution of the silicone, the excess wiped off with a piece of felt, and the coated suture cured by passing through a curing tunnel in which the coated silk is heated to 130° C. for three minutes. The silk suture may be sterilized by heating, as desired, but before use. About 12% by weight of the silk of the silicone remains in the coating.

EXAMPLE 5

The silicone rubber sold as Dow-Corning "Silastic 9711" is milled with 4.2% of benzoyl peroxide for five minutes, cut into small pieces, covered with xylene, and soaked overnight. The swollen material is stirred with additional xylene to obtain a 20% solids concentration. Braided silk prepared as described in Example 1 is passed through the silicone in xylene, wiped with a piece of white

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felt, then cured for one minute each at temperatures of 100° C., 125° C., and 150° C. The silk picks up about 10% by weight of silicone solids. The silk suture is heat sterilized before use. The thus prepared suture is used in operations to suture tissues after surgery. The suture is found to be satisfactory and causes a minimum of tissue irritation and deleterious after-effects.

A pigment or dyestuff may be added to the coating solution if desired. Such coloration of the coating is particularly useful for synthetic filaments which are difficult to color.

EXAMPLE 6

A multi-filament size 3-0 braided polyester suture was coated in two passes with a silicone rubber bath containing 17% silicone solids dispersed in xylene. The coating and curing procedure was as described in Example 5. The suture picked up 2.9% by weight of silicone solids. The polyester suture was non-capillary.

EXAMPLE 7

A multi-filament 2-0 silk suture was braided using 16 carriers each containing 3 end 15 denier silk; a core of 14 ends 20-22 denier silk; a pick count of 50; and a total denier of 966. The construction is of the type shown in FIGURE 3. The braided suture was coated with a methyl phenyl polysiloxane which contains about 72% methyl groups and 28% phenyl groups. The coating bath contained 35% silicone solids in xylol. The excess coating was wiped off with a piece of sponge rubber and the coating was cured for one minute each at temperatures of 100° C., 125° C., and 150° C. The silk picked up 7% by weight of silicone solids for one coat. A second coat under the same conditions yielded a total pick up of 12%. The silk at both coating levels was non-capillary, had good bond and showed good resistance to brooming. Surgeon's knots tied in the silk broke before slipping.

EXAMPLE 8

A multi-filament spun, or twisted, 3-0 silk suture was coated with a methyl-phenyl polysiloxane, processed and cured as in Example 7. The spun and twisted silk had a silicone pick up that ranged from 7% for a single coat to 12% for a double coat. The silk did not broom or bush and the filaments were bonded together, so that a needle could be readily threaded.

EXAMPLE 9

A multi-filament size 3-0 braided nylon suture was coated in two passes in a silicone rubber bath containing 17% silicone solids dispersed in xylene. The coating and curing procedure was that described in Example 5. The nylon suture picked up 4.5% by weight of silicone solids and was non-capillary. Good results were obtained when used in surgery.

EXAMPLE 10

A multi-filament braided 3-0 suture was coated with a bath containing 30% solids of a silicone resin commercially sold as Dow-Corning 804. This resin is a comparatively short chain silicone resin containing both phenyl and methyl substituents on the silicone atoms. Added to this bath was a plasticizer amounting to 20% of the weight of the silicone solids. The silk was immersed in this bath, the excess silicone wiped off with sponge rubber and the silicone was cured in a tunnel for one minute each at temperatures of 100° C., 125° C., and 150° C. The silk for a single coat had a silicone pick up of 7% of the weight of the silk. Silk with two coats had a pick up of 12% silicone resin. Silk coated in this resin bath and the added plasticizer had good hand, was non-capillary and did not broom. Plasticizers used were alkyl aryl phosphates, phthalates, sebacates, citrates, epoxies and polymeric dimethyl siloxanes. The polysiloxanes containing larger proportions of aryl groups require larger amounts of plasticizers. The

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pick up can be readily varied by the pressure on the wipers. A slower cure at a lower temperature gives a good coating. A more rapid cure is generally preferred, as the cure most conveniently takes place in a tunnel, and if a slower cure is used the tunnel must be longer for a given production rate and hence is more expensive.

1 claim:

1. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 6-0; picks per inch 40; denier of raw silk used 112; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

2. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 5-0; picks per inch 40; denier of raw silk used 252; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

3. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 4-0; picks per inch 40; denier of raw silk used 378; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

4. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 3-0; picks per inch 40; denier of raw silk used 630; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

5. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 00; picks per inch 50; denier of raw silk used 966; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

6. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 0; picks per inch 50; denier of raw silk used 1560; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments.

7. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 6 to 11% of its length, immersing the braided silk in a xylene solution of a polymerizable silicone, wiping the braided silk suture, whereby there is a silicone pick up of about

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10% to 20% by weight, and drying and polymerizing said silicone.

8. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 6 to 11% of its length, immersing the braided silk in a solution of a polymerizable silicone rubber containing a catalyst, wiping the braided silk suture, whereby there is a silicone pick up of about 10% to 20% by weight, and drying and polymerizing said silicone by heat, of at least about 150° C. for at least about 30 seconds, thereby also decomposing the catalyst.

9. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 6 to 11% of its length, immersing the braided silk in non-toxic volatile hydrocarbon solvent solution of a polymerizable silicone rubber containing a catalyst, wiping the braided silk suture, drying and polymerizing said silicone, re-immersing in said solution, re-wiping the suture, whereby there is a total silicone pick up of about 10% to 20% by weight, and drying and polymerizing said silicone by heat, of at least about 150° C. for at least about 30 seconds, thereby also decomposing the catalyst.

10. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 6-0; picks per inch 40; denier of raw silk used 112; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

11. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 5-0; picks per inch 40; denier of raw silk used 252; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

12. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 4-0; picks per inch 40; denier of raw silk used 378; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

13. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 3-0; picks per inch 40; denier of raw silk used 630; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

14. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction: U.S.P. size 00; picks per inch 50; denier of raw silk used 964; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

15. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, with high density, having approximately the following construction:

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U.S.P. size 0; picks per inch 50; denier of raw silk used 14560; and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said coating weighing from 10% to 20% of the weight of the silk filaments.

16. A surgical suture comprising a plurality of individual filaments in coordinate configuration, the filaments being banded together to hold the filaments in a unitary strand, and hence non-brooming, having a coating on each filament of a non-toxic, physiologically inert, polymeric silicone, whereby the suture is non-capillary and is inert towards living tissue, the weight of said silicone being from 10% to 20% of the weight of the uncoated filaments.

17. A surgical suture comprising a plurality of individual filaments selected from the group consisting of silk, nylon, polypropylene and stretched oriented polyester, the external filaments being in braided configuration, having a tight braid, and low pick count, with high density, thereby imparting surgically handleable characteristics to the uncoated suture, and a coating on each filament of a non-toxic physiologically inert polymeric silicone, whereby the suture is non-capillary and is inert towards living tissue, the weight of said silicone being from 10% to 20% of the weight of the uncoated filaments.

18. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, and low pick count, with high density, thereby imparting surgically handleable characteristics to the uncoated suture, and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, whereby the suture is non-capillary and is inert towards living tissue, the weight of said silicone being from 10% to 20% of the weight of these uncoated filaments.

19. A surgical suture comprising a plurality of individual silk filaments in coordinate configuration, each filament having thereon a coating of a polymethyl-polyphenyl siloxane, at least the final polymerization being *in situ*, the weight of said silicone being from 10% to 20% of the weight of the uncoated filaments, whereby these suture is non-capillary and is inert towards living tissue, and the siloxane coating causes the filaments to adhere to each other, and thereby be free from brooming, and which suture, when tied in a surgeon's knot, breaks rather than slips, on pulling in tension.

20. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 6 to 11% of its length, immersing the braided silk in a solution of a polymerizable silicone, wiping the braided silk suture, whereby there is a silicone pick up of an amount sufficient to render the finished suture non-capillary and not more than 20% of the weight of the uncoated filaments, and drying and polymerizing said silicone.

21. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 6 to 11% of its length, immersing the braided silk in a solution of a polymerizable silicone rubber containing a catalyst, wiping the braided silk suture, whereby there is a silicone pick up of an amount sufficient to render the finished suture non-capillary and not more than 20% of the weight of the uncoated filaments, and drying and polymerizing said silicone by heat, of at least about 150° C. for at least about 30 seconds, thereby also decomposing the catalyst.

22. The method of making surgical sutures comprising braiding a plurality of filaments of silk into a hard dense core, washing the gum from the braided silk, drying the braided silk, dry stretching the braided silk about 5 to 11% of its length, immersing the braided silk in non-toxic

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volatile hydrocarbon solvent solution of a polymerizable silicone rubber containing a catalyst, wiping the braided silk suture, drying and polymerizing said silicone, re-immersing in said solution, re-wiping the suture, whereby there is a total silicone pick up of an amount sufficient to render the finished suture non-capillary and not more than 20% of the weight of the uncoated filaments, and drying and polymerizing said silicone by heat, of at least about 150° C. for at least about 30 seconds, thereby also decomposing the catalyst.

23. A surgical suture comprising a plurality of individual filaments in coordinate configuration, the filaments being bonded together to hold the filaments in a unitary strand, and hence non-brooming, having a coating on each filament of a non-toxic, physiologically inert, polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments, and the suture is inert towards living tissue.

24. A surgical suture comprising a plurality of individual filaments selected from the group consisting of silk, nylon, polypropylene and stretched oriented polyester, the external filaments being in braided configuration, having a tight braid, and low pick count, with high density, thereby imparting surgically handleable characteristics to the uncoated suture, and a coating on each filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments, and the suture is inert towards living tissue.

25. A surgical suture comprising a plurality of individual silk filaments, the external silk filaments being in braided configuration, having a tight braid, and low pick

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count, with high density, thereby imparting surgically handleable characteristics to the uncoated suture, and a coating on each silk filament of a non-toxic physiologically inert polymeric silicone, said silicone being present in an amount at least sufficient to impart non-capillarity and not more than 20% of the weight of the uncoated filaments, and the suture is inert towards living tissue.

26. A surgical suture comprising a plurality of individual silk filaments in coordinate configuration, each filament having thereon a coating of a polymethyl-polysiloxane, at least the final polymerization being in situ, the weight of said silicone being an amount sufficient to render the finished suture non-capillary and not more than 20% of the weight of the uncoated filaments, and said suture is inert towards living tissue, and the siloxane coating causes the filaments to adhere to each other, and thereby be free from brooming, and which suture when tied in a surgeon's knot, breaks rather than slips, on pulling in tension.

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RICHARD A. GAUDET, Primary Examiner.

JORDAN FRANKLIN, Examiner.

United States Patent (19)

Perciaccante et al.

(11) **4,047,533**(45) **Sept. 13, 1977**

[54] **ABSORBABLE SURGICAL SUTURES
COATED WITH
POLYOXYETHYLENE-POLYOXYPROPY-
LENE COPOLYMER LUBRICANT**

[75] **Inventors:** Vincent Anthony Perciaccante, Long
Island City; Henry Patrick Landi,
Yorktown Heights, both of N.Y.

[73] **Assignee:** American Cyanamid Company,
Stamford, Conn.

[21] **Appl. No.:** 724,804

[22] **Filed:** Sept. 20, 1976

[51] **Int. Cl.:** A61L 17/00

[52] **U.S. Cl.:** 128/335.5; 128/1 R;
428/375

[58] **Field of Search** 128/1, 335.5; 428/275

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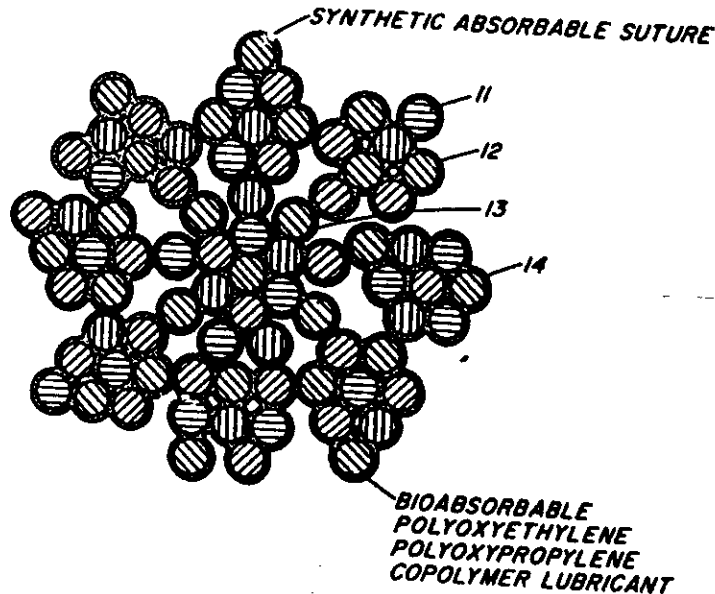
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Primary Examiner—Leland A. Sebastian
Attorney, Agent, or Firm—Charles F. Costello, Jr.

[57] **ABSTRACT**

The handling characteristics, including particularly the knot run-down, of synthetic absorbable surgical sutures and tissue drag characteristics are improved by a coating of a lubricating film of a bioabsorbable copolymer having polyoxyethylene blocks and polyoxypropylene blocks, and which bioabsorbable copolymer has a molecular weight such that it is pasty to solid at 25° C.

23 Claims, 2 Drawing Figures



DePuy Mitek, Inc. v. Arthrex, Inc.
C.A. No. 04-12457 PBS

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U.S. Patent

Sept. 13, 1977

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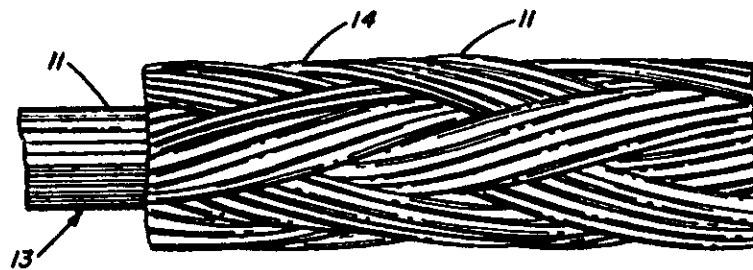
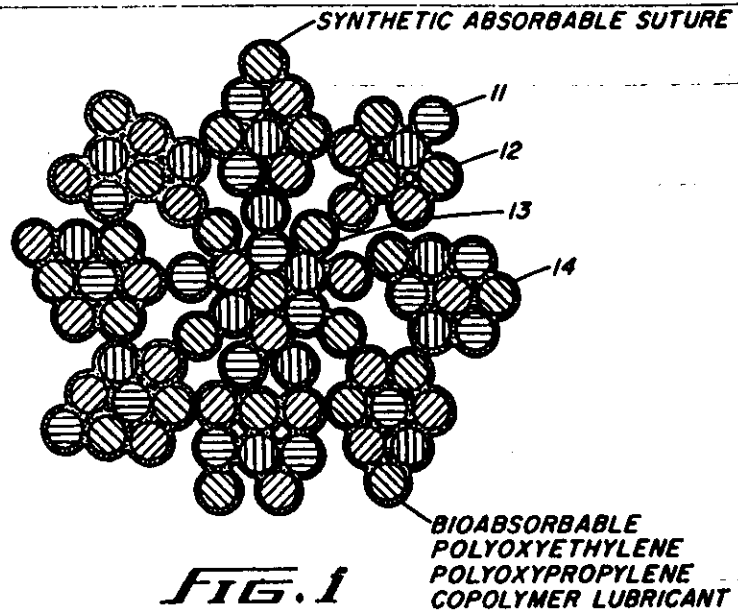


FIG. 2

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ABSORBABLE SURGICAL SUTURES COATED WITH POLYOXYETHYLENE-POLYOXYPROPYLENE COPOLYMER LUBRICANT

BACKGROUND OF THE INVENTION

The handling characteristics of surgical sutures encompass many factors, some of which factors are at least in part inconsistent or seemingly inconsistent. There is a constant effort to improve the handling characteristics. Among the more important of the handling characteristics are those associated with knot run-down. In many surgical procedures it is necessary that a knot be tied in a suture when the knot is deep inside a surgical or natural opening. For instance, a dental surgeon may need to tie a knot inside a patient's mouth. An intravaginal hysterectomy requires suturing in restricted quarters. One technique frequently used is to tie a square knot that can be run-down from an exterior location where the knot is first tied to lie against tissue with a desired degree of tightness. The knot is snugged down so that it is holding with a degree of firmness chosen by the surgeon for a particular situation and then additional throws are tied down against the first throws of the square knot. In some instances, the first throw is a double twist followed by a single throw to form a surgeons knot, with additional throws to form additional square knots on top as needed. As contrasted with the ease of placement, is the necessity of knot security. Each though it is desired that it be easy to tie a knot, it is mandatory that the knot hold without slipping for an acceptable length of time. With buried absorbable sutures, of course, the suture including the knot is eventually absorbed, and the knot need only hold until the tissue is adequately regenerated. This can be merely a few hours for certain types of skin incisions, up to requirements of the order of 15 to 28 days for many types of internal knots. If strength for a longer time or permanent reinforcement is needed, non-absorbable sutures may be used.

Some suture materials are so smooth that a knot runs down very readily and frequently becomes readily untied. Other sutures are of materials in which the knot tends to "lock-up" or refuse to run-down so that it is difficult to snug-down the throws against the tissue and only a few throws are needed, and security is not a problem. Knots in constantly moving tissue, such as adjacent to the heart, have a much greater chance of becoming untied than knots in quiescent tissue such as knots holding together a wound inside a plaster cast.

The problem of improving suture performance under varied conditions has been the subject of much research over a prolonged period.

PRIOR ART

U.S. Pat. No. 1,234,031 — Jan. 22, 1918, Davis, SUTURE AND METHOD OF MAKING THE SAME, shows a braided collagen suture immersed in collagen or glue to cause close adhesion of the braid, to fill up the interstices and provide a smooth uniform coating.

U.S. Pat. No. 2,576,576 — Nov. 27, 1951, Cresswell and Johnstone, LUBRICATED THREAD, shows a lubricated multifilament collagen thread using as a lubricating film a phosphatide such as lecithin. The lecithin should be applied at the time of coagulation or regeneration of collagen as effective lubrication is not

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obtained if the lubricant is incorporated by adding to a finished thread.

U.S. Pat. No. 2,734,506 — Feb. 14, 1956 - Nichols et al. SILK SUTURES AND LIGATURES shows using poly(alkyl methacrylate as a coating for silk sutures, and a hot coating die system.

U.S. Pat. No. 3,187,752 — June 8, 1956 — Glick, NON-ABSORBABLE SILICONE COATED SUTURES AND METHOD OF MAKING, shows silk or other non-absorbable synthetic filaments such as nylon, cotton or linen coated with a silicone which gives a more inert suture and reduces capillarity.

U.S. Pat. No. 3,209,589 — Oct. 5, 1965 — Schlatter, YARN FRICTION MEASURING INSTRUMENT, describes a machine for measuring the friction of a yarn sliding over itself and describes the variation of friction with speed, and the "slip-stick" variety at slow speeds.

U.S. Pat. No. 3,297,033 — Jan. 10, 1967 - Schmitt and Pollstina, SURGICAL SUTURES, shows synthetic surgical sutures of polyglycolic acid and discloses that the surfaces of the fiber can be coated with a silicone, beeswax, or the like to modify the handling or the absorption rate.

U.S. Pat. No. 3,390,681 — July 2, 1968, Kurtz, POLYESTER SUTURE HAVING IMPROVED KNOTTING CHARACTERISTICS, shows improving the knotting characteristics of a polyester such as one formed from a dicarboxylic acid and a diol (Dacron) by depositing on the fibers a polytetrafluoroethylene (Teflon). This patent discloses many of the problems in suture knots, and is hereby incorporated by this reference hereto. This patent also shows the accepted practice of classing "ligatures" under "sutures" for patent disclosure purposes.

U.S. Pat. No. 3,565,077 — Feb. 23, 1971, Glick, DENSIFIED ABSORBABLE POLYGLYCOLIC ACID SUTURE BRAID, AND METHOD FOR PREPARING SAME, shows a suture construction using polyglycolic acid filaments with a compacted structure and a reduced void fraction.

U.S. Pat. No. 3,815,315, June 11, 1974, Glick, ETHYLENE OXIDE STERILIZATION OF MOISTURE SENSITIVE SURGICAL ELEMENTS shows the desirability of maintaining surgical elements of polymers subject to the hydrolytic degradation to non-toxic, tissue-compatible, absorbable components, such as polyglycolic acid sutures, in a desiccated condition in an air tight container impervious to moisture vapor. Suitable desiccating cycles and foil containers to give product which are storage stable for years are disclosed.

U.S. Pat. No. 3,867,190 — Feb. 18, 1975, Schmitt and Epstein, REDUCING CAPILLARITY OF POLYGLYCOLIC ACID SUTURES, shows the coating of polyglycolic acid surgical sutures with a copolymer of from 15-85% glycolic acid with 85-15% lactic acid which coating fills the interstices of a multi-filament polyglycolic acid suture. Example 10 discloses the coating as minimizing capillarity, and improving run-down. Thicker coatings increase stiffness. This patent has 38 references to earlier prior art on sutures and methods of making them, and related fields and is incorporated herein by this reference thereto. A divisional of said 3,867,190 is Ser. No. 489,004, July 16, 1974, REDUCING CAPILLARITY OF POLYGLYCOLIC ACID SUTURES, now U.S. Pat. No. 3,982,543 dated Sept. 28, 1976.

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U.S. Pat. No. 3,896,814 — July 29, 1975 — Vivien and Schwartz, COLLAGEN BASED THREADS, shows a collagen or catgut thread which is flexibilized by having therein water and a hygroscopic agent such as a glycerol or a glycol or a low molecular weight (up to 400 m.w.) liquid polyalkylene oxide, and which may additionally be coated with a lipoid or a silicone for surface lubricity.

U.S. Pat. No. 3,942,532 — Mar. 9, 1976 — Hunter and Thompson — BRAIDED SUTURE, discloses an adaptation of an INSTRON Universal Testing Instrument using an oscillographic recorder, to use a single throw between two suture strands to measure surface roughness, as an indication of the ease of sliding a single throw knot down the suture into place, there called "tie-down performance". A coating of 0.4 percent to 7 percent of the suture weight of an aliphatic polyester such as a condensate of adipic acid and 1,4-butanediol having a molecular weight of about 2,000-3,000 is recommended.

U.S. Ser. No. 691,749, filed June 1, 1976 — Casey and Epstein — NORMALLY-SOLID BIOABSORBABLE, HYDROLYZABLE, POLYMERIC REACTION PRODUCT, discloses the use of transesterification product of poly(1,4-propylene diglycolate) and polyglycolic acid and other trans-esterification products of polyglycolic acid and a polyester of diglycolic acid and an unhindered glycol to coat sutures to improve knot run-down and other suture characteristics.

The coating, coloring and conditioning of surgical sutures with polymeric materials in general is well-known. Silicones, wax, polytetrafluoroethylene, and other polymers have been used. Specific coating materials with unique advantages to give improved sutures are constantly being sought.

SUMMARY OF THE INVENTION

It has now been found that the knot run-down characteristics, handleability, tie-down performance and tissue drag characteristics of braided, twisted or covered multifilament synthetic absorbable sutures may be improved by coating with a lubricating biologically absorbable copolymer having polyoxyethylene blocks and polyoxypropylene blocks.

Absorbable polyglycolic acid sutures are described in U.S. Pat. No. 3,297,033, supra. Other synthetic absorbable sutures which absorb in living tissue may be coated with improved results. At present absorbable sutures meeting with market acceptance are those in which the degradation or absorption in tissue results from the hydrolytic degradation of glycolic acid ester linkages. Such materials are presently being sold under the trademarks DEXON® and VICRYL®. The present invention may be used with other synthetic absorbable surgical sutures, described in the prior art, and as they are developed. With synthetic absorbable sutures the problem of a coating to improve knot run-down characteristics is made more difficult by the requirement that the coating must be non-toxic and absorbable.

Absorbable or bioabsorbable as applied to the coating, refers to a coating which by hydrolytic or enzymatic degradation, or by its inherent characteristic, has such molecular weight and solubility properties that it is absorbed from the surface of the suture and is eliminated by the subject either unchanged or in hydrolyzed or degraded form. The exact mechanism of the disposition of the coating in mammalian tissue is not critical

to the understanding of the present invention, as long as the coating is non-toxic.

It is also found that the lubricant coating not only aids in the knot run-down characteristics but increases the smoothness and flexibility of the sutures so that they may be more easily drawn through the skin and other tissues during placement of the suture. This reduction in friction is called reduced tissue drag.

Another unexpected and unobvious advantage of the present lubricant coating in that the lubricant copolymers are absorbed from the suture within a few days. The coating that aids in friction reduction in tissue drag and lubricates in knot placement also causes the knot to slip more readily. When the lubricant is comparatively rapidly absorbed in living mammalian tissue, the resistance of the knot to slippage or untying due to tissue movement is soon increased. As the wound heals the knot security actually improves, up to the time that the synthetic absorbable suture loses strength preliminary to absorption.

The absorbable coating is one or more of a group of compounds having blocks of polyoxyethylene and blocks of polyoxypropylene in their structure. For simplicity and ease of description these compounds are taught, drawn and treated as if there were merely two or three blocks in the chain. However, it is to be understood that non-significant quantities of polyoxypropylene may be present in the polyoxyethylene block and minor quantities of polyoxyethylene may be present in the polyoxypropylene block. From the methods of manufacture it would appear that there may be and probably are such minor admixtures present in the chain. The commercially available grades are acceptable and found to have a low and acceptable degree of toxicity.

The present lubricants may be indicated as having the formula:



where one of R_1 and R_2 is methyl and the other hydrogen, and n and m are sufficiently large that the compound is pasty to solid at 25° C., R is the residue of a relatively low molecular weight reactive hydrogen compound having from 2 to about 6 reactive hydrogen atoms and having not over 6 carbon atoms in said compound, and c is the number of reactive hydrogens on the compound forming R . Those compounds which are at least pasty at 25° C. are preferred because they adhere better to the synthetic absorbable polyfilamentary suture. There is not a sharp cut off, but in general as the materials become more pasty or solid, their effectiveness improves.

The lubricant compounds and methods of manufacture are described at length in certain prior art. The Pluronic in general are described in U.S. Pat. No. 2,674,619, Apr. 6, 1954, POLYOXYALKYLENE COMPOUNDS, L.G. Lundsted. These are referred to as a cogenetic mixture of conjugated polyoxypropylene-polyoxyethylene compounds and are further described therein.

Certain nitrogen containing polyoxyethylene detergent compositions which are here useful as lubricants are described in U.S. Pat. No. 2,979,528, Apr. 11, 1961, NITROGEN-CONTAINING POLYOXYALKYLENE DETERGENT COMPOSITIONS, L.G. Lundsted. Column 4, lines 44-58 of this patent disclose

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that the oxypropylene chains may have a small amount of ethylene-oxide therein and vice versa. Because of the sources of ethylene oxide and propylene oxide, usually from petroleum fractions, it is to be expected that in commercial practice complete rectification to chemically pure compounds is not obtained. Fortunately the commercial grade may be used on absorbable sutures with excellent results. Said 2,979,528 also points out that as polymers, all molecular species are far from identical—some chains are shorter, some are longer, but on the average the materials are as indicated and it is the physical properties of the lubricants, not the molecular weight spread of the components, which are important.

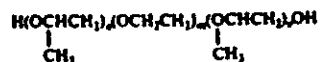
U.S. Pat. No. 3,036,118, May 22, 1962, MIXTURES OF NOVEL CONJUGATED POLYOXYETHYLENE-POLYOXYPROPYLENE COMPOUNDS, D. R. Jackson and L. G. Lundsted, has much disclosure on the addition of polyoxyethylene groups and polyoxypropylene groups to reactive hydrogen compounds having from 2 to 6 reactive hydrogen atoms and not over 6 carbon atoms per molecule. Among other such compounds are listed the group consisting of aliphatic polyhydric alcohols, alkylamines, alkylene polyamines, cyclicamines, amides, and polycarboxylic acids, oxyethylene groups and oxypropylene groups. The reactive hydrogen compound serves as a chain initiator and can be present in such a small proportion that it has minor significance in its own right and serves mainly as a foundation on which the predominantly polyoxyethylene or polyoxypropylene blocks may be added in the chosen order. Whereas Patent 3,036,118 claims primarily the Reverse Pluronics in which the polyoxyethylene chains are attached to the nucleus or initiating reactive hydrogen compounds, in the present invention either the Reverse Pluronic with the polyoxyethylene in the center or the regular Pluronics with the polyoxypropylene in the center or the Tetratics with nitrogen in the center may be used for lubricant purposes.

Because the chemistry is previously known, and to avoid unnecessarily extending the length of the present disclosure, the disclosures of each of these three patents is herein hereby incorporated by this reference thereto.

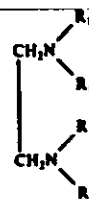
These lubricating bioabsorbable copolymers are often classed as surface active agents as the polyoxyethylene blocks are predominantly hydrophylic and the polyoxypropylene blocks are predominantly hydrophobic. The materials have been sold by the Wyandotte Chemical Company under the trademark of PLURONICS for the formula:



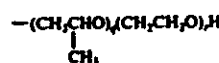
where x, y and z are whole numbers. REVERSE PLURONICS for the formula:



where n, m and o are whole numbers and TETRATICS for the formula:



where R₁ is



where q and r are whole numbers.

For the present purposes as synthetic absorbable suture lubricants, the values of x, y, z, n, m, o, q and r are such that the lubricants are pasty to solid at 25° C.

The pastes are opaque semi-solids with melting points above room temperature—preferably above about 40° C.

Those classed as Pluronics are particularly useful for the present invention.

The physical characteristics of these lubricant compounds are affected by their total molecular weight and by the percentage of polyoxyethylene in the molecule. References are made to the commercially available compounds for purposes of convenience. Those which are liquid normally have an L as a primary designator, those which are pasty have a P and those which are solid have an F. For the Pluronics, the first number indicates the typical molecular weight of the polyoxypropylene hydrophobic portion with a number 3 being about 950; 4 being about 1200; 5 being about 1450; 6 about 1750; 7 about 2050; 8 about 2250; 9 about 2750; 10 about 3250; 11 about 3625 and 12 about 4000. The second digit indicates the approximate percentage of the polyoxyethylene hydrophylic units in the total molecular, in units of 10. Thus for example, the formulations of certain commercially available products is approximately that shown in Table I.

As all compositions are mixtures, all values are approximate, and values are subject to some rounding.

Additional data is given in The Journal of the American Medical Association, volume 217, pages 469 to 470 (1971) where the new nonproprietary name of POLOXAMER is established for these compositions as direct food additives.

TABLE I

PLURONIC	Average Molecular Weight	M.W. of each Polyoxyethylene Block	Units of each x and z	% Polyoxyethylene	M.W. of Polyoxypropylene Block	Units of y	M.P. °C.
F-38	3000	2000	46	80	930	16	45
F-48	8350	1300	75	80	1,750	30	52
F-77	6600	2300	52	70	2,050	35	48
P-35	4600	1200	27	90	2,250	39	40
F-37	7700	2700	62	70	2,250	39	49
F-44	10800	4300	97	80	2,250	39	54
F-98	13500	5400	122	80	2,750	47	55
F-108	14400	5600	128	80	3,150	54	57

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TABLE I-continued

F-127	12500	4300	98	75	3,900	67	56
REVERSE PLURONIC			M.W. polyethylene units of m block		M.W. polyoxy- propylene block		Units of n and O
10R8	1,000	2000	45	65%	362	9	46
17R8	4,330	2600	39	60%	870	15	33
25R8	9,000	3250	74	57%	1,290	22	56

TETRONIC	Average	Approximate Molecular Weight of In-	Approximate	Molecular Approximate	Approximate	Average Approximate length	
	Molecular	dividual Polyox- ethylene Block	% Polyox- ethylene	dividual Polyox- propylene Block	Polyoxypropylene	Units of r of chains per block	Units of q
707	12,000	2312	74	673	26	52.5	11
908	26,100	5588	85	925	15	127	15.9
1107	14,300	2438	67	1173	33	55.4	20.2
1307	18,600	3213	69	1423	31	73	24.3
1508	27,000	5063	75	1673	25	115	28.5

In general, the Pluronics with a molecular weight range of from about 4,750 to 16,250 are waxy solids. The polyoxypropylene portion has a molecular weight of 950 to 4,000 and the polyoxyethylene content of about 60-80%.

The pastes in general have a total molecular weight ranging from 3,500 to 5,700 with a polyoxypropylene molecular weight range of 1,750 to 6,500 and polyoxyethylene content of 30 to 50%. The transitions from wax to paste to liquid are not sharp.

COATING

The synthetic absorbable suture is conveniently coated by several conventional procedures including:

Melt Coating

The uncoated suture is placed in a split die whose orifice corresponds to diameter specifications for the particular size suture to be coated. The die is then clamped in a heating block and the polyoxyethylene-polyoxypropylene lubricant bioabsorbable copolymer placed in the die. The die is raised to a temperature about 20° C. above the melting point of said copolymer and after the copolymer has melted, the suture to be coated is slowly pulled downward through the molten material in the die and collected on a take-up spool. The spool is mounted directly below the die a sufficient distance to allow solidification of the coating. A cooling tunnel or a blast of cooling air may be used to increase production speeds. Nichols et al. 2,734,506, supra, describes one useful apparatus for coating.

Solution Coating

The polyoxyethylene-polyoxypropylene lubricant bioabsorbable copolymer is dissolved in chloroform. About twice the percentage by weight is used for coating solution as is desired on the final sutures. A feed loop such as a loop of wire or a ceramic is threaded with the uncoated suture, after which the feed loop is then submerged in the solution and the suture is passed down through the feed loop. It may be passed through a die whose diameter is such that after drying a suture will have the desired diameter. The suture is pulled slowly through the solution and at least partially dried in a drying tunnel. The drying is finished after the suture is wound on a spool. Because variations in equipment, speed, and temperature affect the pick-up of the lubricant bioabsorbable polymer, the concentration in the coating is adjusted based on a preliminary run or experience.

During the following the application of the coating to the synthetic absorbable sutures, contact of the filaments with moisture, or water vapor is minimized. The

final coated suture is thoroughly desiccated before packaging in a moisture proof container, such as a metal foil envelope, for long term storage stability. U.S. Pat. No. 3,814,315 supra, discloses methods of dry packaging and sterilizing, and is hereby incorporated by this reference thereto.

Other coating techniques which are well known in the coating of polyfilamentary strands may be used. The techniques used for insulating wire may be adapted for large scale suture manufacture. The above are merely two of the more convenient and well known methods for coating. Details are later illustrated in examples.

Toxicity

The low toxicity of the polyoxyethylene-polyoxypropylene compounds of the present invention are shown in such U.S. Pat. Nos. as 3,450,502 which describes the use of a copolymer having a total molecular weight of about 8,750 in isotonic solutions used as a priming agent in a heart-lung apparatus. In sutures even if a maximum of around 25-30% by weight of the suture of copolymer is used, only a very small amount is placed in the subject.

The low toxicity is shown in the following table.

TABLE II

Pluronic No.	Total Molecular Weight	TOXICITY		LD 50 (gm/kg) in Mice
		Physical Characteristic		
F-38	3000	wax		> 5
F-77	6600	wax		4.3
F-87	7700	wax		1.75
F-68	8350	wax		> 5
F-38	10800	wax		> 5
F-127	12500	wax		2.25
F-98	13500	wax		> 5
F-106	14400	wax		1.25
P-45	3400	paste		0.83
P-84	4200	paste		0.4
P-83	4600	paste		0.53
P-94	4600	paste		0.6
P-101	4950	paste		1.4
P-104	5850	paste		0.75
P-123	5750	paste		2.7
P-105	6500	paste		3

The polyoxyethylene-polyoxypropylene compositions used as the lubricant bioabsorbable copolymers have been used in food products; and have been the subject of studies as to their elimination from a mammalian body. In general, they are eliminated in the urine fairly rapidly, and within 48 hours nearly all have been eliminated from the blood stream.

If some of the lubricant bioabsorbable copolymer is trapped in braid pores of a suture, the rate of diffusion into the blood stream may be reduced and hence the

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time for elimination somewhat increased. The molecular weight is small enough that the lubricant bioabsorbable copolymers may be eliminated unchanged, although some degradation may occur before elimination. The important thing is that the lubricant bioabsorbable copolymer has no deleterious effect upon healing tissues adjacent to the sutures, and being removed from the surface of the suture by absorption by the body, knot security is improved. As soon as suture placement is completed, the knot run down and tissue drag reduction function is complete, and as the lubricant bioabsorbable copolymer is removed from the suture, knot security improves.

Definitions in the suture and textile trades are sometimes ambiguous or confused. As herein used:

A "filament" is a single, long, thin flexible structure of a non-absorbable or absorbable material. It may be continuous or staple.

"Staple" is used to designate a group of shorter filaments which are usually twisted together to form a longer continuous thread.

An absorbable filament is one which is absorbed, that is digested or dissolved, in living mammalian tissue.

A "thread" is a plurality of filaments, either continuous or staple, twisted together.

A "strand" is a plurality of filaments or threads twisted, plaited, braided, or laid parallel to form a unit for further construction into a fabric, or used per se, or a monofilament of such size as to be woven or used independently.

The term "suture" is used to include the term "ligature" as technically a suture is used with a needle whereas the ligature is merely used to tie without being placed by a needle.

A finished suture has a needle attached and is sterile and ready for use in surgery. For purposes of convenience in nomenclature, the term "suture" is frequently used to refer to the same strand before it is coated and before it is packaged and sterilized. Context indicates whether it is the sterile suture ready for use, or the suture in a manufacturing step which is referred to.

The strand of the suture is used as the basis for weight in determining the quantity of material that is placed on the synthetic absorbable polymer strand in forming the absorbable surgical suture.

The quantity of the lubricating bioabsorbable copolymer is from about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer based on the weight of the uncoated strand forming the suture. It is not necessary that the coating be continuous as a discontinuous coating on the surface aids in reducing friction and chatter. A larger quantity may be present if the lubricating bioabsorbable copolymer penetrates inside the strand, with the various filaments themselves being partially or totally covered.

The wide range of coating weight permits adaptation of the present sutures to many varied uses. Because the strand to be coated to form the suture may have considerable variation in surface roughness, due to the mechanical structure, i.e. braid or twist, etc. as well as being made from filaments which are less than 2 denier per filament to more than 6 denier per filament, with the finer filament sizes giving a smoother surface; and because the filaments may be stretched after the suture is manufactured or in heat treatment, the surface roughness basically can vary. The smoother surfaces require less of the lubricating bioabsorbable copolymer for analogous degrees of slippage.

The various surgical techniques used interact with the desired degree of lubrication. For any given type of knot, a larger quantity of lubricant which for a particular technique increases the ease of run-down, also increases the ease of the knot running back or slipping, called knot security. For some surgical procedures it is highly desirable that the knot be very free in running down, even though the knot slips more readily.

A surgeon in tying knots is confronted with the interaction between the method of tying the knot and the ease of slipping. If a suture is comparatively well lubricated, the surgeon can use a square knot, which is run down readily; with additional squared throws for knot security. On the other hand, if the suture is less well lubricated, the surgeon can use a double half-hitch or some other type of knot which moves more readily to run the knot down to position, after which these double half hitch can be pulled to square the knot, or additional throws can be thrown down against the knot to give adequate knot security. Thus the surgeon can either adapt his knot technique to a particular suture, or can get sutures whose surface lubricity is best adapted to the technique which the surgeon desires to use. Generally, there is an adaptation of each to the other. The surgeon attempts to get a suture whose characteristics are those which he prefers, and then adapts his knot tying techniques to the sutures that he has at the time. Some surgeons make very successful knots with stainless steel wire using a knotting technique that is adapted to such a wire which has very poor run-down. Others prefer a much more readily run-down well-lubricated suture.

Additionally the location of use has influences. Sometimes a suture in passing through tissue picks up tissue fluids. The suture may be coated with tissue fluids which are either fresh or partly dry at the time the knot is tied. In some surgical techniques it is necessary to preplace the sutures, and tie the suture after the coating of tissue fluids on the suture has a chance to become at least partially dried.

Because the ease of knot run-down and knot security are somewhat opposite, it is necessary for the surgeon to use additional throws or such knots as will hold under the particular conditions of a selected surgical procedure. By changing the quantity of the lubricant bioabsorbable copolymer, the run-down can be modified to suit a using surgeons preference.

The time of use of the knots can be quite varied. Some surgeons use a suture to ligate bleeders in a wound with a retention requirement of 30 minutes or less. Such knots can be removed as the surgical procedure is complete, and before wound closure. Others leave the absorbable knots in the tissue even though there is no likelihood that a bleeder would reopen. For such usage, a suture which retains strength for 30 minutes is adequate. For wound closure and some other uses, it is desired that the synthetic absorbable suture maintain strength for at least 15 days to 4 weeks.

Because the present lubricating bioabsorbable copolymer is removed from the suture in living tissue, as the lubricant is removed the knot security increases and after 48 hours more or less, knot security is greatly improved.

The examples following should show the effects of certain different coating and quantities under certain conditions.

The requirements of surgery are extremely varied, and various coating weights permit adaptation of synthetic absorbable sutures to different conditions.

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In general, if the surgeon desires a better lubricated suture, a larger quantity of the lubricating bioabsorbable copolymer is used and conversely if the surgeon is willing to accept slightly reduced knot run-down and tissue drag characteristics in favor of greater knot security, the coating level is reduced in favor of this particular compromise.

Usually from 2 percent to 8 percent of the lubricant bioabsorbable copolymer gives a useful range of compromise between the ease of knot run-down and knot security.

A usage of about 5 percent by weight of Pluronic F-68 is a preferred compromise between the knot run-down and knot security requirements for 2 to 6 denier per filament braided sutures of polyglycolic acid.

In the Drawings:

FIG. 1 is a cross-section of a synthetic absorbable suture having on the surface thereof a bioabsorbable polyoxyethylene polyoxypropylene copolymer lubricant.

FIG. 2 is a drawing of a suture showing the parallel filaments in the core and the braided sheath. The lubricant coating appears on the surface.

The drawings are diagrammatic and representative. The filaments 11 of the synthetic bioabsorbable suture are at best some what jumbled in actual configuration but are illustrated as patterned in a somewhat idealized style. The coating 12 of the lubricant bioabsorbable polyoxyethylene-polyoxypropylene copolymer is shown much exaggerated. At a level of from 0.1 to 25 percent, the coating would be so thin as to merely be represented by a blurred line if to accurate scale.

In FIG. 2 the core 13 of the braided suture consists of parallel filaments and the sheath 14 consists of a plurality of filaments, typically braided in configuration. The type of braid shown is representative and diagrammatic. The visibility and appearance of the coating varies depending upon the observational technique used to inspect the suture.

The coating 12 in part may bridge the gap between the individual filaments in the finished suture. Depending upon the quantity of coating used, the bridging may be more or less complete but complete filling is not necessary. If the coating level is increased, knot run-down continues to be improved, but knot security is compromised.

EXAMPLE 1

Run Down and Chatter Test

A set of 2/0 USP XIX (diameter 0.339 mm, maximum) polyglycolic acid sutures braided from a 2 denier per filament extrusion, was coated with 7 levels of Pluronic F-68 and a blank, that is no coating, then subjected to a square knot run-down test.

In this test, the suture is tied with a square knot around a cylinder with a 4 inch periphery. The loop thus formed is slipped off the cylinder and placed in the testing machine jaws. The knot is subjected to running-down by pulling on the original free ends in a testing machine which records the pull on a chart as the knot travels down the suture. There is some chatter or variation in knot run-down tension as the knot travels down the suture. This is graphically plotted. Out of a set of runs with various coating levels, the fraction is indicated in which the maximum force for the knot run-down is within the separate ranges given in the table. All of the knots for coated sutures ran down the full length of the suture without breaking. The knot break-

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ing strength of the suture braid was in a range of 7 to 8 pounds. For uncoated braid, the knot locked up and the suture broke in 9 out of 10 tests.

TABLE III

Knot Run-Down on 2/0 Polyglycolic Acid Sutures With Pluronic F-68 Lubricant	
Coating Level	Fraction of trials where maximum resistance was:
	0-1 1-2 2-3 3-4 4-5 5-6 6-7 lbs.
(percent)	
0.0	broke before run-down in 9 out of 10
1.9	2/10 2/10 4/10 2/10
2.8	2/10 3/10 2/10 3/10
3.9	1/10 1/10 4/10 2/10 3/10
5.0	3/10 2/10 2/10 2/10 1/10
6.2	2/10 3/10 2/10 3/10
7.4	1/11 1/11 4/11 3/11
8.0	3/10 2/10 3/10
The maximum force for run-down decreases steadily with increasing level. Lower coating levels on a different batch of braid showed	
0.51%	1/10 2/10 2/10 3/10 2/10
1.09%	3/10 1/10 3/10 1/10
1.53%	3/10 1/10 1/10 1/10 1/10 1/10

For these coatings, the braid was run through a solution of Pluronic F-68 at a concentration of about twice the percentage of coating on the suture in chloroform.

With other braid constructions and other sizes, the relative ease of knot run-down may be greater or less for the same quantity of coating, or conversely the quantity of the coating may be adjusted to give the desired knot run-down values.

The quantity of the Pluronic in the solvent may be varied, and solvents other than chloroform may be used.

Other organic solvents such as methyl alcohol, ethyl alcohol, isopropyl alcohol, methylene chloride, warm xylene (about 60° C.), tetrahydrofuran, acetone, dimethylformamide, dimethyl sulfoxide, mixtures thereof, and other similar solvents for the lubricant may be used for coating. Flowing the solution onto a moving strand, and letting the surplus drip off is another useful coating technique.

A small amount of water increases the solubility of the lubricants, and aids in coating, but the time of contact with water of the suture should be minimized so that if moisture is present in the coating system, the sutures should be dried and desiccated promptly.

In general it is more convenient to use the solvent coating system at levels below 10 percent pick-up and use a heated die at above about 10 percent pick-up.

EXAMPLE 2

A series of runs was made using a coating of two commercial Pluronics F-68 and F-127 on 2/0 size sutures of 6 dpf braided absorbable polyglycolic acid sutures. The coatings were applied by a solution of the Pluronic in chloroform. The concentration of the Pluronic in the solution used for coating is approximately twice that obtained in the braid. A solution containing about 2.8% Pluronic F-68 in chloroform results in about 1.4% Pluronic F-68 on the braid. An adjustment in concentration can be made to secure any desired level. The strand being coated was braided for a 2/0 size suture using a 6 denier per filament extrusion of polyglycolic acid. An uncoated suture strand of the same lot was used as a control. A standard ATLAB yarn Friction Tester Model CS-151-026, Custom Scientific Instruments, Inc. Whippany, New Jersey 07981, with a Hewlett Packard Model 321 dual channel amplifier recorder was used to record the tension of the strand

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feeding into the tester, and coming out of the yarn tester. The chatter factor is the ratio of maximum pull (T_2) to the feed tension (T_1) minus the minimum pull (T_3) to the feed tension, i.e. $(T_2/T_1) - (T_3/T_1)$. The values for friction are of (T_2/T_1) to start slipping.

The values of particular interest are the ratios and percent reduction. With other types of test devices, the numerical values may change, but the relative ratios as

Tests on knot security are dependent on the exact technique of tying knots.

A representative and typical run on knot security showed for a series of tests on size 2/0 polyglycolic acid sutures of 2 denier per filament construction with 4.79% of Pluronic® F-68 coated thereon and different knots, the force in pounds to slip knots or break without slipping to be:

Run	Square Knot	Square + 1 Throw	Square + 2 Throws	Surgeons Knot	Surgeons + 1 Throw	Surgeons + 2 Throws
1	1.70	2.95				
2	2.05	3.90	Broke	Broke	7.90	Broke
3	4.20	4.05	Broke	6.15	5.15	Broke
4	0.70	3.40	Broke	3.70	Broke	Broke
5	3.95	Broke	Broke	3.35	Broke	Broke
Average	2.54	—	—	1.40	—	—

an index of improvement are analogous.

In this test, an uncut strand, coated as indicated, was used for the test. For use as a suture, such strand is cut to length, needled, packaged and sterilized using conventional techniques. The friction and chatter is more readily measured on continuous lengths.

Reduction in static friction, chatter and the coefficient of friction are shown for typical coating levels, and sutures in Table IV.

EXAMPLE 3

A series of runs, including blank, were made with solutions of the Pluronic® R bioabsorbable lubricant copolymers in chloroform, using the procedures of Example II. The following Table V shows the improvement obtained in chatter and friction with a series of polymers and concentrations.

TABLE IV

POLYGLYCOLIC ACID BRAID
Size 2/0

Run No.	Pluronic Coating	Level %	Static Friction	% Reduction	Chatter Factor	% Reduction	Coeff. of Friction $\times 10^{-2}$	% Reduction
1	Blank	0	3.11		0.50		6.109	
2	Blank	0	3.29		0.60		6.274	
3	F-68	1.39	2.78	13.1	0.30	45.5	5.766	7.0
4	F-68	1.93	2.55	20.3	0.19	65.3	5.468	11.8
5	F-68	4.44	2.54	20.6	0.31	43.6	4.900	20.9
6	F-68	7.29	2.70	15.6	0.33	40.0	5.084	17.9
7	F-68	8.09	2.59	19.1	0.25	54.6	5.424	12.5
8	F-127	1.38	2.55	20.3	0.33	40.0	4.938	20.3
9	F-127	1.57	2.63	17.8	0.24	56.4	5.539	10.6
10	F-127	2.56	2.97	7.2	0.27	30.9	6.104	1.50
11	F-127	5.37	2.76	13.8	0.32	41.8	5.689	8.2
12	F-127	5.62	2.82	11.9	0.40	27.3	5.617	9.4
13	P-127	5.62	2.87	10.3	0.29	47.3	6.007	3.1
14	P-127	8.14	2.81	12.2	0.29	47.3	5.891	4.9
15	F-127	9.83	2.74	14.4	0.29	47.3	5.621	9.3

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TABLE V

POLYGLYCOLIC ACID BRAID
Pluronic® Size 2/0 - 6 denier per filament

Braid	Run	Coating	Level (%)	Static Friction	(%) Reduction	Chatter Factor	(%) Reduction	Coeff. of Friction $\times 10^{-2}$	(%) Reduction
Uncoated	16			3.92		0.31		8.189	
Uncoated	17			3.45		0.21		7.503	
Uncoated	18			2.87		0.27		6.083	
Uncoated	19			2.87		0.18		6.300	
10297B	20	10R8	2.05	2.51	23.4	0.28		5.077	28
10297B	21	10R8	3.00	2.33	28.9	0.16	34.1	4.932	31
10297B	22	10R8	3.96	2.31	29.5	0.21	13.6	4.753	33
10297B	23	10R8	5.31	2.41	26.5	0.23	5.4	4.962	30
10297B	24	10R8	7.49	2.39	27.1	0.25		4.843	32
10297B	25	25R8	2.55	2.34	28.6	0.16	34.1	4.962	30
10297B	26	25R8	3.85	2.40	26.8	0.15	38.3	5.162	27
10297B	27	25R8	6.29	2.23	32.0	0.15	38.3	4.662	34
10297B	28	25R8	7.15	2.31	29.5	0.13	46.5	4.990	30
10297B	29	25R8	8.74	2.37	27.7	0.11	54.7	5.175	27
10297B	30	31R4	2.18	2.53	22.8	0.15	38.3	5.520	22
10297B	31	31R4	3.42	2.53	22.8	0.17	30.0	5.466	23
10297B	32	31R4	4.51	2.57	21.6	0.14	42.4	5.652	23
10297B	33	31R4	5.53	2.61	20.4	0.17	30.0	5.705	20
10297B	34	31R4	7.26	2.51	23.4	0.11	54.7	5.782	19
10297B	35	17R8	2.12	2.45	25.3	0.19	21.8	5.218	27
10297B	36	17R8	3.13	2.45	25.3	0.25		5.019	30
10297B	37	17R8	5.02	2.33	28.9	0.20	17.7	4.782	33
10297B	38	17R8	6.32	2.36	28.0	0.25		4.723	34
10297B	39	17R8	8.60	2.33	28.9	0.15	38.3	4.962	30

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EXAMPLE IV

A braided polyglycolic acid strand, of a size to form a 2/0 USP suture is dipped in a 10% solution of Pluronic F-68 in chloroform, and dried. The pick-up is about 3% by weight of the weight of the strand itself.

The dried coated strand is cut into 54" segments, needled, packaged, sterilized and dried in accordance with conventional procedures.

The thus prepared sutures were used in surgical procedures. When used to approximate tissue at a wound, a suture is placed in an appropriate location, and tied with a square knot. The square knot readily ran down to pull the edges of the wound to the degree of tightness desired by the using surgeon. The suture shows low tissue drag, and excellent knot run down. When a knot is at a desired final location, three additional squared throws are placed to secure the knot. Knots buried in tissue have the lubricant bioabsorbable copolymer removed from the suture surface within 48 hours, which gives additional knot security. The suture itself maintains tissue retaining strength for at least 15 days, and is substantially absorbed in 90 days.

Whereas exemplified and tested with square knots, the ease of knot run-down and reduced tissue drag are useful in most suture placements and for knot retention. The amount of coating, and the relative values for knot run-down and reduced tissue drag, is variable to suit the requirement of a particular surgical situation.

The needling, packaging and sterilizing of the coated sutures is in accordance with conventional procedures.

We claim:

1. An absorbable surgical suture having improved knot run-down characteristics and reduced tissue drag comprising a polyfilamentary synthetic absorbable polymer strand having thereon a thin lubricating coating of a lubricating absorbable copolymer comprising polyoxyethylene blocks and polyoxypropylene blocks to aid run-down and handleability, said bioabsorbable copolymer having a molecular weight such that it is pasty to solid at 25° C.

2. The suture of claim 1 in which the lubricating bioabsorbable polymer has the formula:



where one of R₁ and R₂ is methyl and the other hydrogen, and n and m are sufficiently large that the compound is pasty to solid at 25° C., R is the residue of a relatively low molecular weight reactive hydrogen compound having from 2 to about 6 reactive hydrogen atoms and having not over 6 carbon atoms in said compound, and c is the number of reactive hydrogens on the compound forming R.

3. The suture of claim 1 in which the lubricating bioabsorbable copolymer has effectively the formula:



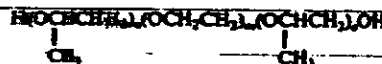
where x, y and z are sufficiently large that the lubricating bioabsorbable copolymer is pasty to solid at 25° C.

4. The suture of claim 3 in which the lubricating bioabsorbable copolymer has a molecular weight of about

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8350 and x and z are about 75 and y about 30, and the melting point is about 52° C.

5. The suture of claim 1 in which the lubricating bioabsorbable copolymer has effectively the formula:

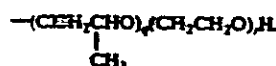


where n, m and e are sufficiently large that the lubricating bioabsorbable copolymer is pasty to solid at 25° C.

6. The suture of claim 1 in which the lubricating bioabsorbable copolymer has effectively the formula:



where R₃ is



where q and r are sufficiently large that the lubricating bioabsorbable copolymer is pasty to solid at 25° C.

7. The suture of claim 1 in which the synthetic absorbable polymer strand is of a tissue absorbable polymer subject to hydrolytic degradation to non-toxic tissue compatible absorbable components, and which polymer has glycolic acid ester linkages.

8. The suture of claim 3 in which the synthetic absorbable polymer strand is of a tissue absorbable polymer subject to hydrolytic degradation to non-toxic tissue compatible absorbable components, and which polymer has glycolic acid ester linkages.

9. The suture of claim 4 in which the synthetic absorbable polymer strand is of a tissue absorbable polymer subject to hydrolytic degradation to non-toxic tissue compatible absorbable components, and which polymer has glycolic acid ester linkages.

10. The suture of claim 7 in which the tissue absorbable polymer is polyglycolic acid.

11. The suture of claim 8 in which the tissue absorbable polymer is polyglycolic acid.

12. The suture of claim 9 in which the tissue absorbable polymer is polyglycolic acid.

13. The suture of claim 1 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

14. The suture of claim 2 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

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15. The suture of claim 3 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

16. The suture of claim 4 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

17. The suture of claim 7 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

18. The suture of claim 8 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

19. The suture of claim 9 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

20. The suture of claim 10 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubri-

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cating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

21. The suture of claim 11 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

22. The suture of claim 12 in which the lubricating coating is about 0.1 to 25 percent by weight of the lubricating bioabsorbable copolymer of the weight of the uncoated strand forming the suture, whereby both chatter and friction are reduced sufficiently that a square knot is movable on the suture with control of a wound edge.

23. A method of closing a wound in living tissue which comprises: sewing edges of a wound in living tissue with the sterile absorbable surgical suture of claim 1,

tying the suture into a square knot, running down the square knot to approximate the tissues in a desired location, placing additional throws on the square knot, and within less than about 48 hours bioabsorbing and removing the lubricant absorbable copolymer from the suture thereby increasing knot security and, leaving the absorbable surgical suture in living tissue until the suture strand is absorbed by living tissue during the healing process, the suture providing useful tissue retention strength for at least 15 days and absorption being substantially complete within 90 days.

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